A TEXT-BOOK

OF

ANALYTICAL CHEMISTRY

FOR

B. Sc. Students

By

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PREFACE

To the First Edition

The present book is expected to meet the demands of a B. Sc. student of the Indian Universities, especially of the Universities of Allahabad, Agra, Banaras, Delhi, Saugor and Lucknow. Though much of the syllabus is common, there are important characteristic departures too. Some of the universities do not insist upon organic preparations or physical experiments. Some of them do not demand the identification of insoluble inorganic substances, and some have their own peculiar way of organic identifications. It is thus difficult to satisfy everybody. But it is hoped that this book, though suggestive and tentative would be helpful to a great extent. The book does not dispense with the experience of an able teacher and guide. It leaves a free scope to the student also for proper systematisation.

A large number of examination questions, as well as numerical exercises form special feature of the book.

In the end, we express gratitude to our colleague and friend Dr. Ram Charan Mehrotra, M.Sc., D. Phil., for his valuable suggestions and help.

S. PRAKASH
R. D. TIWARI

July 5, 1945.

To the Second Edition

The book has been thoroughly revised. The semi-micro, and spot tests have been incorporated. The emphasis in the present edition has been laid on ionic equations. Solved numerical exercises have been added, and the question papers have been brought up-to-date.

S. PRAKASH
R. D. TIWARI

January 29, 1948.

To the Fifth Edition

Since the changes introduced in the fourth edition of the book were very much welcome to our readers, we have introduced a few more organic preparations and physical experiments in the present edition. We have also incorporated in this edition some additional quantitative estimations.

S. PRAKASH.
R. D. TIWARI.

March 20, 1959.

To the Sixth Edition

We have pleasure in introducing another edition of this book to our young readers. The text has been carefully revised, and it is expected that it would meet the demands of our undergraduate students of the Indian Universities.

S. PRAKASH
January 1, 1962. R. D. TIWARI.

To the Seventh Edition

In this edition, we have introduced as an appendix, a systematic treatment for Semimicro Analysis. Some simple inorganic preparations have also been given.

S. PRKASH
August 25, 1963. R. D. TIWARI.

To the Eighth Edition

The Semimicro Analysis, given in the previous edition as an appendix, has been treated as a separate part, and more details have been given. A few more physical concepts have been incorporated. The present edition has been considerably revised and improved to meet the demands in general of all our University B.Sc. students in this country and abroad.

S. PRAKASH
June 15, 1965 R. D. TEWARI

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A TEXT-BOOK OF
ANALYTICAL CHEMISTRY
For B. Sc. Classes

INTRODUCTION

The Analytical Chemistry includes those operations which are performed to determine the constituents of a chemical compound or a mixture of these compounds. It has two aspects—qualitative and quantitative. The syllabus prescribed for the B.Sc. Examination includes the following radicals for the qualitative analysis:—

BASIC—

I	II	III
Silver Lead Mercury (*ous*)	Mercury (*ic*) Lead Bismuth Copper Cadmium Antimony Arsenic Tin	Iron Chromium Aluminium

IV	V	VI
Cobalt Nickel Zinc Manganese	Barium Strontium Calcium	Magnesium Sodium Potassium Ammonium

Acidic—

Acetate Borate Bromide Carbonate Chlorate Chloride	Fluoride Iodide Nitrate Nitrite Oxalate Phosphate	Silicate Sulphate Sulphide Sulphite Thiosulphate

The quantitative analysis, as prescribed in the syllabus of our universities, includes the following estimations *gravimetrically* :—

Iron as ferric oxide.
Copper as cupric oxide.
Barium and sulphate as barium sulphate.
Silver and chloride as silver chloride.
Zinc as oxide.
Chromium as oxide.
Lead as sulphate.
Calcium as oxide.
Aluminium as oxide.
Magnesium as pyrophosphate.

The *volumetric estimations include* :—
Acidimetry and alkalimetry.
Oxalic acid—permanganate titrations.
Ferrous salt—permanganate titrations.
Ferrous salt—dichromate titrations.
Hypo—iodine titrations.
Arsenious acid—iodine titrations.

Iodometric estimations of potassium dichromate, potassium permanganate and copper sulphate.

Silver nitrate—potassium chloride titrations.

Silver nitrate—potassium thiocyanate titrations.

The Organic qualitative Analysis includes the identification of the following substances :—

Chloroform, benzene, ether, phenol, aniline, nitrobenzene, benzaldehyde and ethyl acetate.

Benzoic acid, phthalic acid, salicylic acid, benzamide, acetanilide, naphthalene and iodoform.

Formic acid, acetic acid, formaldehyde, acetaldehyde, acetone, methyl alcohol, ethyl alcohol and glycerine.

Oxalic acid, tartaric acid, succinic acid, citric acid, pyrogallol, resorcinol, glucose, cane sugar, starch, chloral hydrate, acetamide and urea.

The syllabus of some universities also includes large number of organic compounds. The University demands the application of tests characteristic of the groups contained in the above mentioned compounds, and of the compounds themselves, and wherever possible the preparation of a solid derivative in a pure condition.

A few simple organic preparations as prescribed by some of the universities have also been incorporated. A few of the simple physical experiments have been given in an appendix.

Special Reagents for Inorganic Analysis

The ordinary reagents provided in the shelves are the following :—

Reagent	Strength (approx.)	Concentration, grams per litre.	Remarks
Sulphuric acid (conc.)	37 N	1840	Sp. gr. 1·8385.
Sulphuric acid (dil.)	4 N	200	1 part conc. acid to 10 parts of water. (Sp. gr. 1·12).
Hydrochloric acid (conc.)	11 N	400	Sp. gr. 1·2 (39·1%)
Hydrochloric acid (dil.)	4 N	150	1 part conc. acid to 3 parts of water. (Sp. gr. 1·07).
Nitric acid (conc.)	15 N	1000	Sp. gr. 1·520.
Nitric acid (dil.)	4 N	250	1 part acid to 3 parts of water. (Sp. gr. 1·13).
Acetic acid (dil.)	4 N	240	1 part glacial, and 3 parts of water.]
Sodium hydroxide	4 N	160	...
Ammonium hydroxide	4 N	140	Sp. gr. 0·97. 1 part strong ammonia (0·88) to 4 parts of water.
Ammonium chloride	4 M	212	...
Ammonium oxalate	$M/2$	78	$(NH_4)_2C_2O_4,2H_2O$.
Ammonium sulphate	2 N	132	...
Calcium sulphate	0·015M	0·2	Saturated solution.
Ammonium carbonate	2 N		80 g. ammonium carbonate and 32 ml. of 0·88 N. ammonia per litre.

Reagent	Strength (approx.)	Concentration grams per litre.	Remarks
Ammonium molybdate	...	...	See below
Sodium acetate	$2M$	160	270 g. of crystalline salt per litre.
Barium chloride	$M/2$	122	$BaCl_2 . 2H_2O$.
Silver nitrate	$M/10$	17	...
Calcium chloride	M	219	$CaCl_2 . 6H_2O$.
Sodium phosphate	$M/6$	59.6	$Na_2HPO_4 . 12H_2O$.
Ferrous sulphate	solid		$FeSO_4 . 7H_2O$.
Ferric chloride	$M/3$	54	$FeCl_3 . 6H_2O$ (75 g.) +HCl (conc. 5 ml. per litre.)
Lead acetate	$M/2$	190	$(CH_3COO)_2Pb . 3H_2O$.
Potassium ferrocyanide	$M/4$	105.5	$K_4Fe(CN)_6 . 3H_2O$.
Borax	solid	...	$Na_2B_4O_7 . 10H_2O$.
Sodium carbonate	solid	...	Free from chloride and sulphate (test before use).
Manganese dioxide	solid	...	MnO_2.
Potassium chlorate	solid	...	$KClO_3$.
Potassium dichromate	solid	...	$K_2Cr_2O_7$.
Lime water	$N/3$	...	Saturated solution of lime in water.

The following reagents are specially provided on a common side-shelf :—

Ammonium molybdate—150 g. of ammonium molybdate are taken in a litre of water, and to it is added 1 litre of nitric acid, sp. gr. 1·2. Add to this mixture, 100 g. of ammonium nitrate, and allow it to stand overnight and decant.

Yellow ammonium sulphide—10 g. of flowers of sulphur are suspended in a litre of ammonium hydroxide solution (1 vol. liq. ammonia and 2 vols. of water) and H_2S passed.

Ammonium acetate—A strong solution.

Bromine water—A saturated solution—$N/2$.

Potassium iodide—about 16%.

Cobalt nitrate—about $N/2$—72·5 g. per litre.

Mercuric chloride—$N/2$—68 g. per litre.

Stannous chloride—$2N$—118 g. of tin are dissolved in concentrated HCl, and a piece of platinum foil is placed in contact. The solution is diluted to a litre, and if the solution is opalescent, strong HCl is added. The solution is stored in a well-stoppered bottle in contact with metallic tin.

Starch solution—Ought to be freshly prepared (1%).
Alcohol, ethyl.

Silver sulphate solution—$M/20$—15 g. per litre.

SOLIDS—

Copper turnings.	Zinc.
Oxalic acid.	Lead carbonate.
Urea.	Sodium peroxide.
Ammonium chloride.	Lead peroxide.
Sodium nitrite.	Tartaric acid.
Sulphur powder.	Iron nails.
Potassium nitrate.	Sodium bicarbonate.

Sodium nitroprusside—A fresh solution prepared by dissolving a few crystals in water.

Borax solution for glycerine—Just a trace of borax dissolved in a test tube of water and a drop of phenolphthalein aded. Further dilute the pink solution to the desired shade.

Ferrous sulphate—Dissolve a green crystal in a few ml. of water (cold).

Fehling's solution—Dissolve 69.3 g. of pure copper sulphate crystals in 300 ml. of water, with the addition of a few drops of concentrated sulphuric acid. Bottle the solution. (Fehling's solution 1).

Dissolve 350 g. of Rochelle salt (sodium potassium tartrate) and 100 g. of caustic soda in 500 ml. of water. Bottle it up also separately. (Fehling's solution 2).

While using, mix up equal volumes of both the solutions, 1 and 2, as to get a clear blue solution. For ordinary identification, a few drops of the mixed solution would do.

Nessler's solution—Dissolve 32·5 g. of KI in 250 ml. of water. Reserve 10 ml. of the solution. Add the main portion to a cold saturated solution of mercuric chloride, with stirring. A faint precipitate would remain at this stage if mercuric chloride has been sufficiently added. Then add the reserve portion till the precipitate is almost dissolved. Now dissolve 150 g. of KOH in 150 ml. of water, cool and add to the above solution. Dilute it to a litre. Bottle after decantation (keep in dark).

Schiff's reagent—Make a dilute solution of fuchsin and pass sulphur dioxide into the solution till the colour is destroyed.

Phenolphthalein—1 gram of phenolphthalein dissolved in 100 ml. of methylated spirit (warm) and diluted to 500 ml. with spirit and water.

Iodine solution—Dissolve 1 part of iodine in 2 parts of KI along with a few ml. of water. Further dilute it with 50 parts of water.

PHYSICAL PRINCIPLES

Applied to Analytical Chemistry

We shall briefly describe here a number of physical principles involved in Analytical Chemistry, in order to give the student a better understanding of the reactions and tests he would be carrying out in the laboratory.

Types of Reactions—The following are the types of reactions usually met with in Analytical Chemistry.

(*i*) Reactions involving double decompositions, *e.g.*, the formation of sodium sulphate from barium sulphate and sodium carbonate :

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4.$$

(*ii*) Reactions involving simple decompositions, *e.g.*, the formation of calcium oxide from calcium oxalate on heating :

$$CaC_2O_4 = CaO + CO + CO_2.$$

(*iii*) Oxidation reactions, *e.g.*, oxidation of a ferrous salt to ferric by nitric acid :

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

(*iv*) Reduction reactions, *e.g.*, reduction of mercuric chloride by stannous chloride:

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

(*v*) Reactions involving complex formations, *e.g.*, the reaction between a copper salt and potassium cyanide :

$$Cu_2(CN)_2 + 6KCN = 2K_3Cu(CN)_4.$$

(*vi*) Reactions involving surface energy change or structural change, *e.g.*, gelatinous precipitate of copper hydroxide becoming granular on heating and standing, or a partially soluble cobalt sulphide becoming almost insolub e on warming and standing.

The Equilibrium State and the Law of Mass Action—Many chemical reactions are reversible in the sense that under certain conditions they will proceed in one direction, and under other conditions in the opposite direction. A state of equilibrium is reached, as a result of the balancing of two opposite reactions. The conditions of equilibrium can be easily followed by the application of law of mass action.

The law of mass action states that the velocity of a reaction at any instant is proportional to the active concentration of the reaction substances.

If the reaction :

$$A+B+C+\rightleftharpoons A'+B'+C'+\ldots$$

be reversible, then :

$$\frac{[A'][B'][C']\ldots}{[A][B][C]\ldots}=K$$

where the bracketted quantities denote the corresponding concentrations and K is the equilibrium constant. The equilibrium constant depends on temperature and pressure (in the "first type of reactions" involving no change in volume, it is independent of pressure).

Barium sulphate is insoluble in acids yet it can be partially decomposed by boiling with sodium carbonate solution. The reaction is reversible and can be represented by the following equation :—

$$BaSO_4+Na_2CO_3\rightleftharpoons BaCO_3+Na_2SO_4.$$

If a and b be the initial concentrations of barium sulphate and sodium carbonate, and if x molecules have reacted till the equilibrium has been reached, then :

$$\frac{(a-x)(b-x)}{x^2}=K.$$

Now if *b be made* very large compared with a, then $(a-x)$ will be very small, and finally, a will be very nearly equal to x. That is, if the concentration of sodium carbonate be very great, then the whole of barium sulphate will be converted to barium carbonate. Evidently, the greatest concentration of b can be obtained by fusing barium sulphate with sodium carbonate taken in excess.

Effect of Volatility and Insolubility of a Product of Reaction—In many cases, a reaction appears to go to completion instead of to a state of equilibrium. For such cases, Berthollet remarked that this often results from some disturbance of the equilibrium state, by one or more of the products of the reaction *being removed from the sphere of action by their volatility or insolubility*. As soon as they leave the system, passing into gaseous state or depositing as solids, they cease to exert any influence, and the reaction by which they are produced being no longer opposed, cannot become balanced and proceeds to almost completion.

This explains the complete decomposition of calcium carbornate to calcium oxide in an open vessel (though not in a closed one), the complete precipitation of a copper salt as sulphide by hydrogen sulphide, or of the complete precipitation of barium chloride and a soluble sulphate, or the decomposition of sodium chloride with concentrated sulphuric acid.

Ions in Solution. In solutions certain substances known as electrolytes (*i.e.*, those which conduct current) do not behave as complete molecules, but are resolved into simpler entities, known as *ions*. These ions are charged with negative or positive electricity, and are known as *anions* and *cations* respectively (anions move towards *anode* and cations towards *cathode*).

Acids and Bases.—On the classical theory, as propounded by Arrhenius, an acid is defined as a substance which when dissolved in water furnishes hydrogen ions, H^+:

$$HCl \rightarrow H^+ + Cl^-$$

In fact, these hydrogen ions (H^+), also known as *protons*, do not exist free in the aqueous solution. Each proton is bound with one water molecule by coordination with a pair of free or lone electrons on the oxygen of water:

$$H_2O: + H^+ \rightarrow H_3O^+,$$

this very much resembles the formation of NH_4^+ ions :

$$NH_3 + H^+ \rightarrow NH_4^+$$

The H_3O^+ion is known as *hydroxonium* ion.

Thus on this concept, the dissociation of hydrochloric acid in water is represented thus :

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

The dissociation of a polybasic acid like H_3PO_4 proceeds in stages as given below :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$$

or

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{--}$$
$$HPO_4^{--} + H_2O \rightleftharpoons H_3O^+ + PO_4^{---}$$

A *weak acid* is one which furnishes a small concentration of hydrogen ions and which is not completely dissociated.

A *base* is defined as a substance which in aqueous solution furnishes OH^- (hydroxyl) ions.

$$NaOH \rightarrow Na^+ + OH^-$$

The metallic hydroxides (NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$ etc.) are almost completely dissociated, but *ammonia* in aqueous solution furnishes only a weak concentration of OH^-; it is thus known as a *weak base*,

$$NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Brönsted (1923) gave a more general definition of acids and bases. According to him, any substance which donates protons (H^+) is an *acid* and any substance which accepts protons is a *base*.

In an expression

$$A \rightleftharpoons B + H^+$$

A and *B* are termed a *conjugate* acid-base pair. The dissociation of an acid to furnish H^+ is conditional by the presence of a base, i. e., a substance capable of accepting the liberated H^+.

Thus we have the following included on the list of *acids*:

(*i*) the classical acids, with uncharged molecules, as HCl, H_2SO_4, CH_3 COOH etc.

(*ii*) anions as HSO_4^-, $H_2PO_4^-$, HPO_4^-, $HOOC.COO^-$ etc.

(*iii*) ammonium ion, since it shows the equilibrium

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

and hydroxonium ion

$$H_3O^+ \rightleftharpoons H_2O + H^+$$

(*iv*) cations like hydrated aluminium and other metallic ions :

$$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5)OH]^{2+} + H^+$$

Similarly, we have the following bases :

(*i*) uncharged molecules (ammonia and amines) by virtue of the reaction $RNH_2 + H^+ \rightarrow RNH_3^+$

(*ii*) metallic hydroxides, furnishing OH^-

$$OH^- + H^+ \rightarrow H_2O$$

Some substances can function both as acids and bases, and are hence known as *ampholytytes* (such as H_2O, HCO_3^-, $H_2PO_4^-$ etc.)

Protolytic reaction.—An acid is a donor of protons $A_1 \rightleftharpoons B_1 + H^+$; a base is an acceptor of a proton $B_2 + H^+ \rightleftharpoons A_2$. Thus we have on addition of an acid to a base :

$$\underset{\text{acid}_1}{A_1} + \underset{\text{base}_2}{B_2} \rightleftharpoons \underset{\text{acid}_2}{A_2} + \underset{\text{base}_1}{B^1}$$

Therefore the reaction between an acid and a base is called *protolytic* reaction; some such reactions are given below :

Acid$_1$		Base$_2$		Acid$_2$		Base$_1$
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
HSO_4^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$SO_4^=$
NH_4^+	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NH_3
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
HCl	+	C_2H_5OH	$\rightleftharpoons$	$C_2H_5OH_2^+$	+	Cl^-

Dissociation constant.—In the case of most of the electrolytes, the ionisation is incomplete in the sense that the cent per cent molecules do not resolve into ions, a few of them remain undissociated. If a be the fraction dissociated (that is if a be the degree of ionisation), and if one gram-mole of the electrolyte be dissolved in V litres of solution, then for a weak electrolyte (the one which is only feebly ionised) :

$$\underset{1-a}{HA} \rightleftharpoons \underset{a}{H^+} + \underset{a}{A^-}.$$

the application of the law of mass action to this case of equilibrium gives :

$$\frac{[H^+][A^-]}{[HA]} = K.$$

or

$$\frac{a/V \times a/V}{(1-a)V} = K$$

or

$$\frac{a^2}{(1-a)\,V} = K;$$

K is known as the *dissociation constant* of the electrolyte.

Ammonium hydroxide is a weak base, and the ionisation takes place in the following way :—

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-.$$

The dissociation constant is given by :

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K = 1{\cdot}75 \times 10^{-5}.$$

Similarly, for hydrogen sulphide :

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$\frac{[H^+]\ [HS^-]}{[H_2S]} = K = 1{\cdot}75 \times 10^{-8}$$

In the case of polybasic acids as phosphoric acid, there are a number of dissociation constants known as the first, second and so forth They correspond to the various stages of its ionisation :

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad (K_1 = 1{\cdot}4 \times 10^{-2})$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad (K_2 = 2{\cdot}0 \times 10^{-7})$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}. \qquad (K_3 = 3{\cdot}6 \times 10^{-13})$$

The degree of ionisation depends upon temperature and dilution; the increased temperature and the increased dilution give an increased value of the degree of ionisation.

Activity and Activity coefficients. While referring to Ostwald's dilution law, which is based on the application of law of mass action to an equilibrium condition, we presumed that the effective concen-

trations or active masses of the components could be expressed by the stoichiometric concentrations. But in solutions of electrolytes, it is not so. There are electric forces acting between the oppositely charged ions; the ions are not completely free in their movements, and hence they behave as if they were of lower concentration than that calculated stoichiometrically. Each ionic concentration, therefore, ought to be multiplied by a factor, which is termed the *activity coefficient*. The *activity a* of an ion is given by its stoichiometric *concentration c* multiplied by the *activity coefficient*, f

$$a = f \times c$$

Thus for a binary electrolyte

$$AB \rightleftharpoons A^+ + B^-$$

the *thermodynamic dissociation constant* should be expressed in terms of activities and not in terms of stoichiometric concentrations.

$$K_{therm.} = \frac{a_{A^+} \times a_{B^-}}{a_{AB}}$$

where a_{A+} is the *activity* of the ion A^+, a_{B-} of the ion B^-, and a_{AB}, of the undissociated molecule. If their activity coefficients are respectively f_{A+}, $f_{B-}$and f_{AB}, and their stoichiometric concentrations are $[A^+]$, $[B^-]$ and $[AB]$, then

$$a_{A+} = f_{A+} \times [A^+],\ a_{B-} = f_{B-} \times [B^-],\ \text{and}$$

$$a_{AB} = f_{AB} \times [AB]$$

$$K_{therm.} = \frac{[A^+][B^-]}{[AB]} \times \frac{f_{A+} \times f_{B-}}{f_{AB}}$$

Solubility Product—If solid silver chloride is in contact with its saturated solution, we have the two connected equilibria:

$$AgCl\ (solid) \rightleftharpoons AgCl\ (dissolved) \rightleftharpoons Ag^+ + Cl^-.$$

If the law of mass action be applied to ions, we get :

$$[Ag^+][Cl^-] = K[AgCl].$$

But the concentration of the unionised AgCl is constant at a given temperature, if excess of solid AgCl is present. Hence in equilibrium, the product of the ionic concentations is constant at a given temperature. This constant product, *e.g.*, $[Ag^+][Cl^-]$ is called the *solubility product*.

When the product of the ionic concentrations is *equal* to the solubility product, the solution is in *equilibrium* with the solid, since the concentration of unionised salt in solution must be that which is in equilibrium with the solid. If the ionic product is *less* than the solubility product, the solution is *unsaturated* with respect to the solid, and more of the latter dissolves. But if the ionic product is *greater* than the solubility product, *precipitation* of the solid occurs, unless the solution remains supersaturated.

If the most general case of an electrolyte be A_pB_q, dissociating as given below :

$$A_pB_q \rightleftharpoons pA^+ + qB^-$$

then the solubility product of this electrolyte is given by

$$S = [A^+]^p \times [B^-]^q$$

For example, the solubility of silver chromate, Ag_2CrO_4, is $2{\cdot}5 \times 10^{-2}$g./l and therefore, its solubility product is given by:

$$S = [Ag^+]^2[CrO_4^{2-}]$$

The mol. wt. of $Ag_2CrO_4 = 332$, hence the solubility 2.5×10 -2/g./l.

$$= \frac{2{\cdot}5 \times 10^{-2}}{332} \text{ mol./l.}$$

$$= 7{\cdot}5 \times 10^{-5} \text{ mol.}/l.$$

Now 1 mol. of Ag_2CrO_4 would give 2 mols of Ag^+ and 1 mol of CrO_4^{2-}. Therefore,

$$S = [2 \times 7{\cdot}5 \times 10^{-5}]^2 \times (7.5 \times 10^{-5})$$
$$= 1{\cdot}7 \times 10^{-12}$$

In the course of the book, we have given various applications of solubility products. A list of the solubility products of sparingly soluble salts is given at the end of the book.

The solubility product rule may apparently be disturbed when complex ions are formed. For example, if potasium cyanide solution is added to a solution of silver nitrate, a white precipitate of silver cyanide, AgCN, is first produced, since the solubility product $[Ag^+][CN^-] = 2 \times 10^{-12}$ corresponding with the solubility of silver cynide is exceeded. On further addition of potassium cyanide, however, the silver cyanide dissolves, since a complex ion is formed : $AgCN + CN^- = Ag(CN)_2^-$. The silver is contained in the anion, and practically no silver ions are present. The complex ion is, however, slightly dissociated :

$$Ag(CN)_2^- = Ag^+ + 2(CN^-).$$

No precipitate is formed with soluble chlorides, since the silver ion concentration is too small to reach the solubility product, $[Ag^+]$ $[Cl^-]$; but silver sulphide is precipitated on adding sodium sulphide since the solubility product, $[Ag^+]^2 \times [S^=]$ being very small, is reached even with very small concentration of Ag^+ available from the complex ions $Ag\ (CN)_2^-$.

As the solubility of silver chromate is more than that of silver chloride, potassium chromate is used as an indicator in silver nitrate-potassium chloride titrations.

Hydrogen Ion Concentration and Analytical Reacions.—Water may be supposed to be a very weak electrolyte, dissociating as follows :

$$H_2O = H^+ + OH^-.$$

As the concentration of undissociated water is constant in this case, the product $[H^+]\ [OH^-]$ is also a constant. This is known as the *ionisation constant of water* and has a value of $10^{-13.8}$. This ionic product is constant for all aqueous solutions, whether acid, neutral or alkaline. At the neutral point, concentrations of hydrogen ion and hydroxyl ion are equal, each being $10^{-6.9}$. If the hydrogen ion concentration is more than this value, the solution is acidic, and if less, then alkaline.

The concentration of hydrogen ions may be more conveniently represented by minus the exponent of the concentration (the base being 10), and is then usually written as pH. Thus if the hydrogen ion concentration be $10^{-6.9}$, the pH. is 6·9 and so on. A pH numerically less than 6·9 indicates that the solution is acidic, and if the pH be more than 6·9, the solution is alkaline.

Hydrolysis—Salts formed from a strong acid and a strong base are neutral in reactions, but the salts from either a weak acid or a weak base are alkaline or acidic in aqueous solutions. This is due to the fact, that water also behaves as a weak acid or a weak base and reacts upon the salt producing a free acid or a free base. This action of water is called hydrolysis.

The following are types of salts which show the phenomenon of hydrolysis :

(*i*) *The salt of a strong base and weak acid gives alkaline solutions* :—

$$Na^+ + CH_3COOO^- + H^+ + OH^- \rightleftharpoons Na^+ + OH^- + CH_3COOH.$$

(*ii*) The salt of a weak base and strong acid gives acidic solutions :

$$Bi^{3+} + 3Cl^- + 3H^+ + 3OH^- \rightleftharpoons Bi(OH)_3 + 3H^+ + 3Cl^-.$$

(*iii*) The solution of a weak base and weak acid is also hydrolysed, the acidity or alkalinity depending on the relative strengths of the two :—

$$(NH_4)_2CO_3 = 2NH_4^+ + CO_3^{2-}$$

$$\begin{array}{lll} 2NH_4^+ + CO_3^{2-} + 2H^+ + 2OH^- & & \\ \quad \rightleftharpoons 2NH_4OH & + & H_2CO_3 \\ \qquad\quad \upharpoonleft\!\downharpoonright & & \quad \upharpoonleft\!\downharpoonright \\ \quad\ 2NH_4^+ + 2OH^-. & & H^+ + HCO_3^-. \end{array}$$

The hydrolysis of a salt is suppressed by the addition of an acid or an alkali as the case may be. For example, bismuth chloride is not hydrolysed in presence of strong acids, and sodium acetate in presence of alkali solutions. This influence of hydrogen and hydroxyl ions is clear from the reversible reactions given above.

Ionic Equations. In qualitative and quantitative inorganic analysis most of the involved reactions are ionic. Thus the test of chloride involves reaction between the positively charged silver ions and the negatively charged chloride ions to give the non-ionic silver chloride precipitate. Instead of writing the equation as.

$$AgNO_3+NaCl=AgCl+NaNO_3,$$

we shall write in a general way :

$$Ag^++Cl^-=AgCl.$$

In balancing such equations, care must be taken that the *total net charge on the right-hand side of the equation is the same as on the left-hand side.* In the above equation, it is zero on both the sides.

Similarly, the raction between mercuric chloride and stannous chloride: $2HgCl_2+SnCl_2=2HgCl+SnCl_4$, is ionically represented as :

$$2Hg^{++}+Sn^{++}=2Hg^++Sn^{++++}$$

or $$2Hg^{2+}+Sn^{2+}=2Hg^++Sn^{4+}$$

The mercuric ion is reduced to mercurous and the stannous ion is oxidised to stannic. The total net charge on both the sides of the equation is 6.

The reaction betwen oxalic acid and permanganate in presence of dilute sulphuric acid, is :

$$2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O,$$
$$5H_2C_2O_4+5O=5H_2O+10CO_2.$$

This equation is represented in ionic form as follows:—

$$16H^++5C_2O_4^{2-}+2MnO_4^-=2Mn^{2+}+8H_2O+10CO_2$$

The net charge on both the sides is 4. This equation follows from the above two equations, when common ions have been eliminated from both the sides :

$$2K^++2MnO_4^-+6H^++3SO_4^=+10H^++5C_2O_4^=$$
$$=2K^++SO_4^=+2Mn^{2+}+2SO_4^{2-}+8H_2O+10CO_2$$

The students are expected to have a practice of representing equations in the ionic form.

Coprecipitation.—We are familiar with the fact that if barium sulphate is precipitated in the presence of potassium nitrate, the precipitate of $BaSO_4$ is contaminated with a lot of Ba^{2+} ions, which cannot be removed, even by washing many times with water. Ferric ions if present in the medium are also carried down similarly by $BaSO_4$ precipitate. The contamination of a precipitate by a substance that is *normally soluble* under the conditions of precipitation is termed *coprecipitation.* Thus manganese usually gets coprecipitated, if present, along with ferric hydroxide in the Iron Group of qualitative analysis. Similarly, zinc is also coprecipitated along with CuS in the Second Group, even when the solution is acidic (0·2 M of acidity).

Fractional precipitation.—We shall illustrate it by an example. (Mohr's method of estimating chlorides). The chloride ions are titrated with silver nitrate solution, i. e. titrated with Ag^+. The indicator used is a solution of potassium chromate (or chromate ion, CrO_4^{2-}) when silver ion is added for titration to the halide ion containing the indicator there is a possibility of the formation of two sparingly soluble substances, AgCl and $Ag_2 CrO_4$. Their solubility products are:

$$\text{of AgCl} \qquad 1\cdot5\times10^{-10} = [Ag^+][Cl^-] \qquad \text{(i)}$$

$$\text{of } Ag_2CrO_4 \qquad 2\cdot4\times10^{-12} = [Ag^+]^2\,[CrO_4^{2-}] \qquad \text{(ii)}$$

From (i) and (ii), one obtains

$$\frac{[Ag^+]^2[Cl^-]^2}{[Ag^+]^2[CrO_4^{2-}]}=\frac{[Cl^-]^2}{[CrO_4^{2-}]}=\frac{(1\cdot5\times10^{-10})^2}{2\cdot4\times10^{-12})}=\frac{1}{1\cdot1\times10^8} \qquad \text{(iii)}$$

silver chromate will therefore not precipitate unless its concentration or more correctly, the chromate ion concentration is in excess of that given by this equation. It is clear from this that if the original solution contains chloride and a chromate in equivalent proportions, and one adds Ag^+ ions (i.e. silver nitrate solution) drop by drop, silver chloride will be precipitated until CrO_4^{2-} concentration is in excess of the ratio given in equation (iii). After this, silver chromate will be precipitated with traces of AgCl, the equilibrium ratio in (iii) being maintained in the supernatant liquid.

In actual titrations usually we have $[Cl^-]=0\cdot1$ molar, $[Ag^+]=0\cdot1$ molar (0·1 M $AgNO_3$), $[CrO_4^{2-}]=2\times10^{-3}$ molar (i.e. 2 ml. of 0·1 molar K_2CrO_4 solution per 100 ml. of solution). From this it is clear that the precipitation of AgCl is almost complete before the appearance of Ag_2CrO_4 precipitate of a permanent nature.

PART I

Reactions Involved in Inorganic Analysis of

Basic Radicals

Separation of Basic Radicals into Groups

For the purpose of examination of metals by wet tests, they are divided into a number of groups depending upon the solubility of certain salts of these metals under certain conditions.

They are generally classified into six groups:—

First Group or Silver Group—This includes metals, the chlorides of which are insoluble in acidified cold water, and are precipitated from their solutions by the addition of *dilute hydrochloric acid.* They are silver, mercury (*ous*) and lead.

Second Group or Copper-Arsenic Group—This includes metals, the sulphides of which are insoluble in *dilute* hydrochloric acid, and are, therefore, precipitated by passing *hydrogen sulphide* to the filtrate of the First Group. They are mercury, lead, bismuth, copper, cadmium, arsenic, antimony and tin.

Third Group or Iron Group—This consists of metals, iron, chromium and aluminium, the hydroxides of which are precipitated by the addition of *ammonium hydroxide in presence of ammonium chloride* to the filtrate of the Second Group. The hydroxide of manganese is usually coprecipitated in this group.

Fourth Group or Zinc Group—This group includes nickel, cobalt, manganese and zinc, the sulphides of which are insoluble in ammonium hydroxide, and are, therefore, precipitated by passing hydrogen sulphide in the filtrate of the Third Group.

Fifth Group or Barium Group—This consists of barium, strontium and calcium, the carbonates of which are insoluble in ammoniacal solution and are, therefore, precipitated by adding ammonium carbonate solution to the filtrate of the Zinc Group.

Sixth Group or Magnesium Group—This consists of magnesium alone which is precipitated by the addition of sodium phosphate solution to the filtrate of the Fifth Group.

Sodium, Potassium and Ammonium—These three radicals do not fall into any group and are, therefore, to be tested separately by individual tests.

1. Metals of the First Group

SILVER

Silver is usually given as nitrate, but when given as insoluble it is given in the form of halides.

1. With *dilute hydrochloric acid*, a white curdy precipitate of silver chloride is obtained, which is soluble in ammonia :

$$AgNO_3+HCl=AgCl\downarrow+HNO_3,$$

or
$$Ag^++Cl^-=AgCl\downarrow$$
$$AgCl\downarrow+2NH_3=Ag(NH_3)_2Cl.$$

The silver-ammonia complex is soluble in water. The complex again breaks up on the addition of nitric acid in excess and AgCl is precipitated:

$$Ag(NH_3)_2Cl+2HNO_3=AgCl\downarrow+2NH_4NO_3.$$

2. *Potassium chromate* in neutral solution gives a brick red precipitate, insoluble in acetic acid but soluble in dilute nitric acid and in ammonia solution:

$$2AgNO_3+K_2CrO_4=Ag_2CrO_4\downarrow+2KNO_3.$$

or
$$2Ag^++CrO_4^{=}=Ag_2CrO_4\downarrow.$$

The solubility of silver chromate is more than that of silver chloride and hence it is used as an indicator in the $AgNO_3-KCl$ titration.

3. Metallic *zinc* precipitates metallic silver not only from solutions containing silver ions but also from insoluble silver halides in presence of dilute sulphuric acid :

$$2AgBr+Zn=Ag+ZnBr_2,$$

or
$$2Ag^++Zn=Zn^{++}+2Ag.$$

4. Silver nitrate gives a white precipitate of silver thiocyanate with *potassium thiocyanate* :

$$AgNO_3+KCNS=AgCNS\downarrow+KNO_3,$$

or
$$Ag^++CNS^-=AgCNS\downarrow.$$

The reaction is used in the volumetric estimation of silver using ferric alum solution as an indicator.

5. *Spot test*—p-*Dimethyl-amino-benzylidine-rhodanine* is the reagent used for this test which was first proposed by Feigl.

Place a drop of a silver test solution on a spot plate (or on a drop reaction paper). Now add a drop of the reagent. A red reddish violet colour is obtained.

As the reagent also reacts with mercury, copper and lead salts, it can be made specific for silver, by adding to the test solution a 4 per cent. solution of KCN, and then acidifying with dilute nitric acid. With this treatment, only silver gives the reddish-violet coloration.

6. *Dry test*—When heated on charcoal with fusion mixture, silver compounds yield a shining bead of metallic silver.

LEAD

The usual salts given are lead acetate, lead carbonate, lead nitrate and lead sulphate (insoluble).

1. With *dilute hydrochloric acid*, the soluble lead salts give a white precipitate of $PbCl_2$, soluble in hot water, but separates out on cooling, as brilliant needle crystals:

$$Pb(NO_3)_2+2HCl=PbCl_2\downarrow+2HNO_3,$$

or

$$Pb^{++}+2Cl^{-}=PbCl_2\downarrow.$$

2. With *hydrogen sulphide*, the soluble salts, and even the insoluble lead carbonate and chloride, give in *dilute* and *slightly acid* solutions or suspensions a black precipitate of PbS :

$$Pb(NO_3)_2+H_2S=PbS\downarrow+2HNO_3,$$

or

$$Pb^{++}+S^{=}=PbS\downarrow.$$

From *strong* hydrochloric acid solutions, an orange-red precipitate of lead sulphochloride is at first formed :

$$2PbCl_2+H_2S=2HCl+Pb_2Cl_2S.$$

which is decomposed immediately by more of the hydrogen sulphide.

Lead sulphide is decomposed with nitric acid, when heated, to form lead nitrate:

$$3PbS+8HNO_3=3Pb(NO_3)_2+2NO+4H_2O+3S.$$

3. A soluble lead salt gives a precipitate of lead sulphate on the addition of dilute *sulphuric acid*. The precipitation is complete in the presence of ethyl alcohol.

$$Pb(NO_3)_2+H_2SO_4=PbSO_4\downarrow+2HNO_3.$$

This lead sulphate is soluble in ammonium acetate because lead acetate is only feebly ionised in the solution in presence of acetate ions, so much so that whatever ions are available from the solubility of the lead sulphate also disappear on the formation of unionized lead acetate. The solubility of lead sulphate in ammo-

nium acetate is sometimes accounted for by another fact also that a soluble ammonium plumbi-sulphate is formed.

$$PbSO_4 = Pb^{++} + SO_4^{=}$$

$$Pb^{++} + 2CH_3COO^- = (CH_3COO)_2Pb.$$

$$2PbSO_4 + 2CH_3COONH_4 = Pb\ (O.SO_2.ONH_4)_2 + (CH_3COO)_2Pb.$$

This property is also utilised in the identification of lead sulphate when it is given as an insolutble substance.

4. With potassium chromate, a soluble lead salt gives a yellow precipitate of lead chromate, which is insoluble in acetic acid, but is soluble in mineral acids :

$$(CH_3COO)_2Pb + K_2CrO_4 = PbCrO_4 \downarrow + 2CH_3COOK.$$

5. *Potassium iodide* gives a yellow precipitate of lead iodide with a soluble lead salt:

$$Pb(NO_3)_2 + 2KI = PbI_2 \downarrow + 2KNO_3$$

6. *Spot test*—(*a*) The reagent used is either *benzidine* (0·5% in 10% acetic acid) or *tetramethyl-diphenyl methane*. Place a drop of 3% H_2O_2 on drop reaction paper; add a drop of dilute ammonia and immediately a drop of Pb^{++} test solution. Hold the paper in steam for one minute to decompose the excess of H_2O_2. Now add a drop of the reagent. The appearance of blue colour indicates the presence of lead. This test is, however, not specific.

(*b*) *Resorcinol* test—Place a drop of lead solution on spot paper. Now add a drop of dilute ammonia and then a drop of 5 per cent aqueous solution of resorcinol. A blue colour forms in the course of a few minutes.

(*c*) Prepare a solution of 1—2 mg. of *diphenyl thiocarbazone* in 100 mls. of carbon tetrachloride. To the test solution, add a drop of this reagent. A brick-red compound is obtained with lead and other heavy metals. But in presence of KCN and potassium tartrate only lead responds to this test.

Dry test—When heated on charcoal with fusion mixture, lead salts are reduced to metallic lead which leaves a black mark when drawn across a white paper. At the same time a yellow incrustation of PbO is formed on charcoal.

MERCURY (OUS)

The salt usually given is mercurous nitrate or sulphate.

1. *Hydrochloric acid* gives a white precipitate of mercurous chloride:

$$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 \downarrow + 2HNO_3$$

$$Hg_2^{++} + 2Cl^- = Hg_2Cl_2$$

2. The precipitate of mercurous chloride turns black on the addition of *ammonium hydroxide*:

$$\underset{\text{black}}{Hg_2Cl_2+2NH_3 \rightarrow [NH_2-Hg-Cl+Hg]+NH_4Cl}$$

This black residue of NH_2Hg_2Cl changes to a mixture of finely divided mercury and $HgNH_2Cl$ which is also black in colour.

3. A freshly prepared alcoholic solution of *gallic acid* gives an orange colour with a mercurous salt solution. The colour is yellow in dilute solution. No cations of Group I or II interfere with this reaction.

Chemistry of the First Group Analysis

On adding cold dilute HCl to the cold solution of the mixture in water or dilute nitric acid, the chlorides of silver, lead and mercurous mercury are thrown down as white precipitate:

$$Pb(NO_3)_2+2HCl=PbCl_2\downarrow+2HNO_3$$
$$AgNO_3+HCl=AgCl\downarrow+HNO_3$$
$$Hg_2(NO_3)_2+2HCl=Hg_2Cl_2\downarrow+HNO_3.$$

On boiling this mixture of chlorides $(AgCl+PbCl_2+Hg_2Cl_2)$ with water, lead chloride dissolves and can be tested in solution by adding K_2CrO_4 or KI when yellow precipitate of $PbCrO_4$ or PbI_2 separates out.

$$PbCl_2+K_2CrO_4=PbCrO_4\downarrow+2KCl.$$
$$PbCl_2+2KI=PbI_2\downarrow+2KCl.$$

The residue left undissolved on boiling with water is a mixture of AgCl and Hg_2Cl_2. This is treated with ammonium hydroxide, when AgCl forms soluble complex. From the complex, it can be reprecipitated on the addition of HNO_3.

$$AgCl+2NH_3=Ag(NH_3)_2Cl.$$
$$Ag(NH_3)_2Cl+2HNO_3=AgCl\downarrow+2NH_4NO_3.$$

Mercurous chloride also forms a complex with ammonia but this complex is not soluble and is black in colour.

$$Hg_2Cl_2+2NH_4OH=Hg_2NH_2Cl+NH_4Cl+2H_2O.$$

$$Hg_2Cl_2+2NH_3 \rightarrow \underset{\text{black}}{\left[Hg\genfrac{}{}{0pt}{}{\diagup Cl}{\diagdown NH_2}+Hg\right]}+NH_4Cl.$$

The black residue of aminomercurous chloride dissolves in aqua regia or in hydrochloric acid containing a few crystals of potassium chlorate producing mercuric chloride.

$$NH_2HgCl+2HCl=NH_4Cl+HgCl_2$$
$$Hg+2HCl+O=HgCl_2+H_2O.$$

On adding $SnCl_2$, to $HgCl_2$, the latter is reduced first to white Hg_2Cl_2 and then to grey or black Hg.

$$2HgCl_2+SnCl_2=SnCl_4+Hg_2Cl_2 \quad \text{(white)}.$$
$$Hg_2Cl_2+SnCl_2=2Hg+SnCl_4 \quad \text{(grey or black)}.$$

On diluting the solution of $HgCl_2$ and introducing a copper foil, a grey deposit of mercury over copper is obtained.

$$HgCl_2+Cu=Hg+CuCl_2.$$

2. Metals of the Second Group

MERCURY (*ic*)

The substances usually given are mercuric oxide, chloride, sulphate and nitrate. Mercuric sulphide is also given as an insoluble substance.

1. With *hydrogen sulphide*, mercuric salts give a black precipitate of mercuric sulphide :

$$HgCl_2+H_2S=HgS\downarrow+2HCl.$$

or $$Hg^{++}+S^{=}=HgS.$$

This sulphide does not dissolve in yellow ammonium sulphide and in nitric acid, but it dissolves in aqua regia or a mixture of concentrated hydrochloric acid and potassium chlorate.

It should be noted that the precipitate obtained by passing H_2S in solutions of mercuric salts is at first white, then yellow, brown and finally black. The white precipitate is of $Hg_3Cl_2S_2$:

$$3HgCl_2+2H_2S=4HCl+\underset{\text{white}}{Hg_3Cl_2S_2}$$

2. *Stannous chloride* precipitates mercurous chloride when added to a mercuric salt.

$$2HgCl_2+SnCl_2=Hg_2Cl_2\downarrow+SnCl_4.$$

or $$2Hg^{++}+Sn^{++}=Hg_2^{++}+Sn^{++++}$$

With an excess of stannous chloride, we get metallic mercury on further reduction :

$$Hg_2Cl_2+SnCl_2=2Hg+SnCl_4,$$

or $$2Hg_2^{++}+Sn^{++}=2Hg+Sn^{++++}.$$

3. In the acidic solution, mercuric salt gives a grey deposit of metallic mercury on a bright *copper* strip :

$$HgCl_2+Cu=Hg+CuCl_2,$$

or
$$Hg^{++}+Cu=Hg+Cu^{++}$$

4. Mercuric salts with *potassium iodide* give a bright red precipitate of HgI_2.

$$HgCl_2+2KI=HgI_2\downarrow+2KCl.$$
$$Hg^{++}+2I^-=HgI_2.$$

The precipitate is, however, soluble in an excess of potassium iodide solution :—

$$2KI+HgI_2 = K_2HgI_4.$$

or
$$2I^-+HgI_2 = HgI_4^{=}.$$

5. *Spot test—Diphenyl carbazide* in alcohol is the reagent. Place a drop of the carbazide on a spot-plate or on a drop reaction paper. Now add a drop of very dilute nitric acid, and finally, place a drop of the mercuric salt solution. A violet-blue colour indicates the presence of mercuric salt. The test is specific in absence of chromates and molybdates.

LEAD

The reactions have already been explained along with the metals of the First Group.

BISMUTH

The salts usually given are bismuth nitrate, carbonate, subcarbonate and phosphate.

1. *With hydrogen sulphide*—All bismuth salt solutions give brown (blackish) precipitate when hydrogen sulphide is passed through them :

$$2BiCl_3+3H_2S=Bi_2S_3\downarrow+6HCl.$$

or
$$2Bi^{+++}+3S^{=}=Bi_2S_3.$$

This precipitate is insoluble in cold dilute mineral acids, and also in yellow ammonium sulphide. But it readily dissolves in hot dilute nitric acid, and boiling concentrated hydrochloric acid.

$$Bi_2S_3+8HNO_3\rightarrow 2Bi(NO_3)_3+2NO+4H_2O+3S.$$

2. *With ammonia*—Bismuth salt solutions give with an excess of ammonium hydroxide, a white precipitate of bismuth hydroxide (mixed with the basic salt).

$$Bi(NO_3)_3+2NH_4OH=O{=}Bi{-}NO_3\downarrow+2NH_4NO_3+H_2O.$$
$$Bi(NO_3)_3+3NH_4OH=Bi(OH)_3\downarrow+3NH_4NO_3.$$

The precipitate of indefinite composition is soluble in dilute acids :

$$(BiO)NO_3+3HCl=BiCl_3+HNO_3+H_2O.$$

If the precipitate is dissolved in the least quantity of concentrated hydrochloric acid, and then added to a large quantity of water, a white precipitate of bismuth oxychloride, $BiOCl$, is obtained.

$$BiCl_3+H_2O=BiOCl+2HCl.$$

3. *With water*—All bismuth salts are hydrolysed by water, and therefore, they are rendered insoluble in a large quantity of water, (a few drops of the acid solution of bismuth salts to be added to a beaker full of water). Basic salts are precipitated:

$$BiCl_3+H_2O=BiOCl\downarrow+2HCl$$
$$Bi(NO_3)_3+H_2O=BiO(NO_3)\ +2HNO_3$$

These precipitates redissolve on the addition of concentrated acids.

4. *With sodium-stannite reagent*—Take about half a ml. of stannous chloride solution and add to it caustic soda solution. A white precipitate of stannous hydroxide is first obtained, which then dissolves in excess of caustic soda, forming the solution of sodium stannite, Na_2SnO_2 or $Sn\,(ONa)_2$.

$$SnCl_2+2NaOH=Sn(OH)_2+2NaCl,$$
$$Sn(OH)_2+2NaOH=\underset{\textit{stannite}}{Sn(ONa)_2}+2H_2O.$$

On the addition of the sodium stannite reagent to the few drops of the bismuth salt solution or even to the precipitate of $Bi(OH)_3$, an immediate black precipitate is obtained. This is a very sensitive test.

In this reaction, bismuth salts or hydroxide are reduced to free bismuth which gives black precipitate; stannite is oxidised to stannate:

$$2Bi(OH)_3+3Na_2SnO_2\rightarrow 3Na_2SnO_3+2Bi+3H_2O,$$
$$2Bi^{+++}+6OH^{-}+3SnO_2^{=}\rightarrow 3SnO_3^{=}+2Bi+3H_2O.$$

The test should be performed in cold and with not too concentrated caustic soda.

This test can be successfully performed in a depression of the *spot plate* also.

5. *Spot test—Cinchonine potassium iodide* complex is the reagent used for the test. 1 g. of cinchonine is dissolved in 100 ml. of warm water: this is then acidified with 2—3 ml. of strong nitric acid. The mixture is cooled and then about 2 g. of potassium iodide are added.

To a drop of bismuth test solution on a spot plate, add a drop of the above reagent. A red precipitate of the double iodide, BiI_2 [cinchonine]. HI, is formed. The test solution should not be highly acidic.

A mixture of lead, mercury and bismuth can be identified with this reagent. Place two drops of the reagent on the filter paper, and in the centre, one drop of the mixture solution. A white central zone indicates the presence of Hg^{++}. Next to it is the orange-red zone of Bi^{+++}. Then follows the yellow zone of Pb^{++}. The outermost brown zone is of free iodine.

COPPER

The salts usually given are cupric sulphate, chloride, acetate, nitrate, and oxides.

1. *With hydrogen sulphide*—A sufficient quantity of *dilute* hydrochloric should be added before passing hydrogen sulphide through cupric salt solution. On passing the gas, black precipitate of cupric sulphide is obtained :

$$CuSO_4 + H_2S = CuS\downarrow + H_2SO_4,$$

or $$Cu^{++} + S^{=} = CuS\downarrow .$$

(*a*) Copper sulphide is insoluble in small quantities of yellow ammonium sulphide in *cold* but it is *appreciably soluble* in large quantities of yellow ammonium sulphide, specially *on heating*. (It is, however, not soluble in sodium sulphide. It is the ammonium radical with which a soluble complex is formed.)

(*b*) Copper sulphide is soluble in hot dilute nitric acid, forming cupric nitrate :

(*c*) The sulphide is soluble in potassium cyanide, forming potassium cuprous cyanide. If H_2S is passed through this complex salt solution, no precipitate of CuS is obtained.

$$CuS + 2KCN = Cu(CN)_2 + K_2S$$

$$2Cu(CN)_2 = Cu_2(CN)_2 + (CN)_2$$
$$Cu_2(CN)_2 + 6KCN = 2K_3Cu(CN)_4.$$

2. *With caustic soda*—A blue precipitate of cupric hydroxide is obtained with caustic soda in cold. But if concentrated solution of caustic alkali is added in excess and the solution warmed, cupric hydroxide appreciably dissolves.

Cupric hydroxide on warming becomes brownish and finally black, giving dehydrated oxide :

$$Cu(OH)_2 = CuO + H_2O.$$

3. *With ammonia*—When a small quantity of ammonium hydroxide is added, a precipitate of the basic salt, $CuSO_4.Cu(OH)_2$, (a mixture) of copper sulphate and (copper hydroxide), is obtained but if ammonia solution is added in excess, an intense blue solution is obtained. A soluble complex cupri-ammonia salt is formed:

$$CuSO_4 + 4NH_4OH = [Cu\ (NH_3)_4]SO_4 + 4H_2O.$$

If H_2S is passed through this blue solution, the black sulphide is again precipitated. The blue complex is decomposed on the addition of acids. Thus with acetic acid :

$$[Cu(NH_3)_4]SO_4 + 4CH_3COOH = CuSO_4 + 4CH_3COONH_4.$$

Now, in this solution, copper may be tested by potassium ferrocyanide solution.

4. *With potassium ferrocyanide*—Neutral and acidic solutions of copper Salts furnish with dilute postassium ferrocyanide solution, a reddish brown precipitate or colloidal solution of copper ferrocyanide:

$$2CuSO_4 + K_4Fe\ (CN)_6 = Cu_2Fe(CN)_6 + 2K_2SO_4.$$

5. *With potassium iodide*—Cupric salts with potassium iodide solution liberate iodine and precipitate cuprous iodide white.

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

or $$2Cu^{++} + 4I^- = 2Cu^- + 2I^+ + I_2.$$

6. *With potassium cyanide*—(*a*) Cupric salts with potassium cyanide give at first yellow cupric cyanide, which, however, is unstable, and decomposes into white cuprous cyanide and cyanogen :

$$CuSO_4 + 2KCN = Cu(CN)_2 + K_2SO_4,$$
$$2Cu(CN)_2 = Cu_2(CN)_2 + (CN)_2,$$

or $$2Cu^{++} + 4CN^- = 2Cu^+ + 2(CN)^- + (CN)_2.$$

Insoluble white cuprous cyanide dissolves in an excess of potassium cyanide, forming potassium cuprocyanide:

$$Cu_2(CN)_2+6KCN=2K_3Cu(CN)_4.$$

or
$$Cu^+ + 4(CN)^- = Cu\,(CN)_4^{---}$$

(*b*) If potassium cyanide is added to intense blue cuprammonium sulphate (from 3), the blue colour disappears, and colourless solution of potassium cuprocyanide is formed. The reactions may be followed in the following steps :

$$Cu(NH_3)_4SO_4=CuSO_4+4NH_3,$$
$$2CuSO_4+4KCN=Cu_2\,(CN)_2+2K_2SO_4+(CN)_2,$$
$$Cu_2(CN)_2+6KCN=2K_3Cu\,(CN)_4.$$

This complex is ionised in the solution thus:

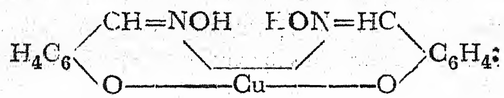
$$K_3Cu(CN)_4 \rightleftharpoons 3K^+ + Cu\,(CN)_4^{---}.$$

But, then for the second dissociation :

$$Cu\,(CN)_4^{---} \rightleftharpoons Cu^+ + 4CN^-$$

the dissociation is so low that no copper ions are available in the solution of potassium cuprocyanide. This accounts for the fact that when hydrogen sulphide is passed through its solution, no precipitation of copper takes place. (Compare this with cadmium cyanide complex).

7. *Spot test* with *salicyl-aldoxime*—Place a drop of test solution on a spot plate and slightly acidify with dilute acetic acid. Then add a drop of the aldoxime solution. A dirty green precipitate appears due to the formation of—



The test is quite specific and sensitive.

Benzoinoxine or *Cupron* is also sometimes used which gives with copper ions (on development with NH_3 vapours) a green colour. The test, however, is specific only in ammoniacal tartrate solutions.

CADMIUM

The salts usually given are cadmium sulphate, chloride, nitrate, acetate and phosphate.

1. *With hydrogen sulphide*—In feebly acidic, neutral or alkaline solutions, cadmium salts give yellow precipitate with hydrogen sulphide.

$$CdSO_4+H_2S=CdS\downarrow+H_2SO_4,$$

or
$$Cd^{++}+S^{--}=CdS\downarrow;$$

(*a*) This precipitate is not soluble in cold dilute sulphuric acid, but is easily soluble in dilute hydrochloric acid (as provided on the shelf, $3N$). It does not precipitate completly until the acid is sufficiently diluted.

(*b*) Cadmium sulphide is soluble in hot dilute nitric acid; Reaction is as follows :—

$$3CdS+8HNO_3=3Cd(NO_3)_2+4H_2O+2NO+3S.$$

(*c*) Cadmium sulphide, when precipitated from halides (chlorides etc.), is intense orange in colour in the beginning due to the formation of sulphochloride;

$$2CdCl_2+H_2S=CdS.CdCl_2+HCl.$$

The colour is lightened by the prolonged action of H_2S.

(*d*) Cadmium sulphide does not markedly dissolve in yellow ammonium sulphide. The weak solutions, however, give colloidal solutions of cadmium sulphide, but in the presence of various salts (usually present as the product of various reactions), the solution precipitates out.

2. *With ammonia*—Cadmium salts give white precipitate of the hydroxide with small quantites of ammonia solution, but this precipitate is soluble in an excess of the reagent :

$$CdCl_2+2NH_4OH=Cd(OH)_2\downarrow+2NH_4Cl,$$
$$Cd(OH)_2\downarrow+4NH_4OH=Cd(NH_3)_4(OH)_2+4H_2O.$$

3. *With potassium cyanide*—With smaller concentrations of potassium cyanide, cadmium salts give white precipitate of cadmium cyanide.

$$CdCl_2+2KCN=Cd(CN)_2\downarrow+2KCl.$$

This precipitate is, however, soluble in an excess of the reagent, forming a complex.

$$Cd(CN)_2\downarrow+2KCN\rightleftharpoons K_2Cd(CN)_4.$$

This salt ionises in the following way :—

first dissociation : $K_2Cd(CN)_4\rightleftharpoons 2K^++Cd(CN)_4^{=}$ . . . (1)
and further,

second dissociation : $Cd(CN)_4^{=}=Cd^{++}+4(CN)^-$ . . . (2)

The dissociation constant for the second reaction is also *pretty high*, and therefore when hydrogen sulphide is passed through the complex cyanide, cadmium sulphide is precipitated.

$$K_2Cd(CN)_4+H_2S=2KCN+CdS\downarrow+2HCN.$$

In this respect, cadmium differs from copper. On this basis, the separation of the two is effected in the analysis.

Spot test with thiosinamine or allylthiourea, NH_2CSNH-$(CH_2CH : CH_2)$—To a drop of the test solution on a glass slide, add a drop of strong solution of NaOH, and then a drop of the reagent. Warm *gently*. A yellow precipitate indicates the presence of cadmium. Copper does not interfere with this test.

Copper and cadmium separation—(*a*) We have already seen that whereas the second dissociation constant of $K_2Cd\ (CN)_4$ is pretty high giving sufficient concentration of available cadmium ions in the solution of this complex, very few, hardly any, copper ions are available from the second dissociation of $K_3Cu(CN)_4$. This is the reason that when hydrogen sulphide is passed through the solutions, containing a mixture of potassium cuprocyanide and potassium cadmium-cyanide, only cadmium sulphide is precipitated, and not copper sulphide.

Thus cadmium is easily detected even in presence of copper.

There is, however, no difficulty in identifying copper in presence of cadmium. The intense blue coloration with ammonia is clear indication of it. This may be further confirmed by the potassium ferrocyanide test.

(*b*) Another method of copper-cadmium separation is based on the observation that whereas copper sulphide is insoluble in even moderately strong hydrochloric acid, cadmium sulphide dissolves in dilute hydrochloric acid (say, 2*N*) also.

Thus, through the mixed solution of cuprammonia and cadmium ammonia complex solutions, pass hydrogen sulphide and get mixed precipitates of copper sulphide and cadmium sulphide. Now to these precipitates, add dilute hydrochloric acid (2*N*). Cadmium sulphide will go into the solution. Separate out copper sulphide by filtration and now dilute the filtrate and pass hydrogen sulphide again. Cadmium sulphide will be precipitated.

ARSENIC

(*a*) *Arsenious Compounds*

Arsenious compounds correspond to As_2O_3 oxide. Usually, the substances given are arsenious acid (As_2O_3) itself and its salt, sodium arsenite, Na_3AsO_3. Whereas, this salt is soluble in water, arsenious acid dissolves only sparingly (about 4%) even on boiling.

Arsenious acid (the same thing as arsenious oxide) dissolves readily in concentrated hydrochloric acid on warming.

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O.$$

Arsenious acid is, however, very readily soluble in caustic soda solution. In case one finds difficulty in preparing acid-solution of this oxide, he should dissolve it in a few drops of caustic soda solution, and then add water and acidify with an excess of acid and proceed further with the analysis.

1. *With hydrogen sulphide*—Arsenious oxide, sparingly dissolved in boiling water, yields yellow colloidal arsenious sulphide on passing hydrogen sulphide, but in presence of acids, this sulphide is precipitated as a flocculent mass.

$$As_2O_3+3H_2S=As_2S_3\downarrow+3H_2O,$$
$$2AsCl_3+3H_2S=As_2S_3\downarrow+6HCl.$$

(*a*) Arsenious sulphide is insoluble even in hot concentrated hydrochloric acid.

(*b*) When heated with concentrated nitric acid, it is oxidised to arsenic acid (the sulphur is simultaneously oxidised to sulphuric acid) :

$$3As_2S_3+28HNO_3+4H_2O=6H_3AsO_4+9H_2SO_4+28NO.$$

The reaction may be easily followed in such steps :—

$$2HNO_3=2NO+H_2O+3O,$$
$$As_2S_3+14O=As_2O_5+3SO_3,$$
$$As_2O_5+3H_2O=2H_3AsO_4,$$
$$SO_3+H_2O=H_2SO_4.$$

(*c*) Arsenious sulphide is soluble in ordinary as well as *yellow ammonium sulphide.* In these cases, only thiosalts are formed :

$$As_2S_3+3(NH_4)_2S=2(NH_4)_3AsS_3,$$

or

$$As_2S_3+3S^{=}=2AsS_3^{---}.$$

As yellow ammonium sulphide contains more of available sulphur, a part of the ammonium thioarsenite is changed to ammonium thioarsenate (corresponding to As_2S_5) :—

$$(NH_4)_3AsS_3+S=(NH_4)_3AsS_4.$$

(*d*) When a solution of arsenious sulphide in ammonium sulphide in acidified with dilute hydrochloric acid, arsenious sulphide is again precipitated.

$$2(NH_4)_3AsS_3+6HCl=6NH_4Cl+As_2S_3\downarrow+3H_2S.$$

The precipitate is mixed with precipitated sulphur also from yellow ammonium sulphide.

$$(NH_4)_2S_x+2HCl=2NH_4Cl+H_2S+(x-1)S.$$

2. *With ammonium molybdate*—All arsenious compounds when heated with concentrated nitric acid yield arsenic acid. H_3AsO_4. The reaction between arsenious sulphide and nitric acid has already been given in 1 (b).

This arsenic acid with ammonium molybdate solution in presence of nitric acid gives crystalline yellow precipitate of ammonium arsenomolybdate (a mixed compound of ammonium arsenate and molybdic oxide MoO_3) :

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3$$
$$= 12H_2O + 21NH_4NO_3 + (NH_4)_3AsO_4 \cdot 12MoO_3 \downarrow .$$

A similar yellow precipitate of ammonium phosphomolybdate is obtained when phosphates are heated with nitric acid and ammonium molybdate.

(*b Arsenic Compounds.*

Arsenic compounds correspond to the oxide, As_2O_5· or the acid H_3AsO_4:

$$As_2O_5 + 3H_2O = 2H_3AsO_4.$$

Salts of these acids are called arsenates, which may be acid, neutral or alkaline :

$$NaH_2AsO_4,\ Na_2HAsO_4,\ Na_3AsO_4.$$

1. *With hydrogen sulphide.* In the beginning, for sometime, acidic arsenate solutions do not give any precipitate with hydrogen sulphide, but if the gas is continuously passed, arsenate is reduced to arsenite, which then gives a yellow precipitate with hydrogen sulphide.

The reduction of arsenic acid to arsenious is accompanied by the appearance of white turbidity, due to the liberated sulphur.

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S.$$
$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O.$$

Usually, it is a mixture of tri and pentasulphides that is obtained.

(*a*) Arsenic pentasulphide is soluble in caustic soda, ammonia and ammonium sulphide solutions. The reactions are similar to those given by arsenious sulphide with the difference that in this case, instead of arsenites and thioarsenites, arsenates and thioarsenates are obtained.

$$As_2S_5 + 6NaOH = Na_3AsSO_3 + Na_3AsS_4 + 3H_2O,$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4,$$

or $$As_2S_5 + 3S^{=} = 2AsS_4^{\equiv}.$$

(*b*) When ammonium thioarsenate is acidified with hydrochloric acid, arsenic pentasulphide is precipitated :

$$2(NH_4)_3AsS_4+6HCl=6NH_4Cl+As_2S_5\downarrow+3H_2S.$$

(*s*) Arsenic pentasulphide with concentrated nitric acid is oxidised to arsenite and sulphuric acid :

$$2HNO_3=2NO+H_2O+3O,$$
$$As_2S_5+20O=As_2O_5+5SO_3,$$
$$As_2O_5+3H_2O=2H_3AsO_4.$$

This arsenic acid gives a yellow precipitate when heated with *ammonium molybdate* in presence of nitric acid.

2. *Gutzeit test* for semimicro analysis—This test depends upon the liberation of arsine, AsH_3, and its subsequent reaction with silver nitrate. Place a few drops of the test solution in the evolution tube; add a few granules of zinc (free from arsenic) and one or two drops of dilute sulphuric acid. Place over the tube a strip of filter paper, moistened with a solution of silver nitrate. A yellow or grey spot will indicate the presence of arsenic. The yellow spot is due to the formation of $AsAg_3{\cdot}3AgNO_3$, which finally, on hydrolysis yields black silver.

$$AsAg_3{\cdot}3AgNO_3+3H_2O=6Ag+H_3AsO_3+3HNO_3.$$

ANTIMONY

Antimony gives three oxides Sb_2O_3, Sb_2O_5, and Sb_2O_4. The trioxide, Sb_2O_3, is soluble in concentrated hydrochloric acid, forming antimony trichloride.

$$Sb_2O_3+6HCl=2SbCl_3+3H_2O.$$

The antimony pentoxide, Sb_2O_5, is also soluble in concentrated hydrochloric acid, forming antimony pentachloride.

$$Sb_2O_5+10HCl=2SbCl_5+5H_2O.$$

The tetroxide is, however, not soluble in even hot contrated hydrochloric acid. It is regarded as one of the sparingly soluble substances.

The usual salts of antimony given are oxides, and antimony sulphate or chloride.

(*a*) *Antimonious Compounds.*

1. *With water*—Antimony salts are hydrolysed in presence of a large excess of water, first to a basic salt, and finally to oxide; they give white precipitates.

$$SbCl_3+H_2O\rightleftharpoons SbOCl\downarrow+2HCl,$$
$$2Sb.O.Cl+H_2O\rightleftharpoons Sb_2O_3+2HCl.$$

These precipitates are soluble in strong acids.

2. *Hydrogen sulphide*—From slightly acidic solutions, hydrogen sulphide gives flocculent orange-red precipitate of antimony sulphide :

$$2SbCl_3+3H_2S \rightleftharpoons Sb_2S_3\downarrow+HCl.$$

This reaction is reversible, as is seen from the fact that antimony sulphide is soluble in concentrated hydrochloric acid (1 : 1). In this respect it differs from arsenic. In order to ensure the complete precipitation of antimony, one has to dilute the solution repeatedly while passing hydrogen sulphide through it.

(Do not dilute the solution from the beginning, otherwise the oxychlorides will be precipitated. Let the hydrogen sulphide pass through for sometime, and then dilute, and again pass the gas).

(*a*) Antimony sulphide is soluble in ordinary ammonium sulphide as well as in yellow ammonium sulphide. The reactions are similar to those of arsenic sulphide.

$$Sb_2S_3+3(NH_4)_2S=2(NH_4)_3SbS_3,$$

or

$$Sb_2S_3+3S^{=}=2SbS_3^{---}.$$

Thus with ordinary ammonium sulphide, ammonium thioantimonite is formed. In yellow ammonium sulphide, there is an excess of sulphur, which converts thioantimonite to thioantimoniate.

$$(NH_4)_3SbS_3+S=(NH_4)_3SbS_4.$$

(*b*) When solutions of thioantimonite and thioantimoniate are acidified with dilute hydrochloric acid, antimony sulphide is again precipitated :

$$2(NH_4)_3SbS_3+6HCl=6NH_4Cl+Sb_2S_3+3H_2S.$$

(*c*) Antimony sulphide dissolves when heated with strong hydrochloric acid.

$$Sb_2S_3+6HCl \rightleftharpoons 2SbCl_3+3H_2S.$$

(*b*) *Antimonic Compounds.*

1. *With water*—White antimonic oxychloride is precipitated if a large excess of water is added to antimonic chloride solution :

$$SbCl_5+2H_2O \rightleftharpoons SbO_2Cl\downarrow+4HCl.$$

This precipitate is soluble in strong acids.

2. *With hydrogen sulphide*—Antimonic salts in fairly acid solutions give orange-red precipitate of a pentasulphide :

$$2SbCl_5+5H_2S=Sb_2S_5\downarrow+10HCl.$$

(*a*) But when the pentasulphide is treated with hot concentrated hydrochloric acid, it is the trichloride which is formed and not the pentachloride.

$$Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + 2S.$$

(*b*) The pentasulphide is soluble in ammonium sulphide solution, forming ammonium thioantimoniate :

$$Sb_2S_5 + 3(NH_4)_2S = 2(NH_4)_3SbS_4.$$

Dilute hydrochloric acid precipitates the pentasulphide again from this solution.

3. *With platinum-zinc couple*—Zinc precipitates metallic antimony from antimony chloride solutions. The reaction is usually done with zinc-platinum couple. In the loop of a platinum wire. a small piece of metal zinc is fastened, and held into the hydrochloric acid solution of antimony chloride. Hydrogen (nascent) is evolved which displaces antimony from the salt and a black deposit of it is observed on platinum wire :

$$SbCl_3 + 3H = Sb + 3HCl,$$

or

$$Sb^{+++} + 3H = Sb + 3H^+.$$

This is a sensitive and convenient test for antimony.

4. *With iron nails*—(*a*)When antimony chloride solution in concentrated hydrochloric acid is boiled along with an iron nail, metallic antimony is precipitated in black flakes (or powder) :

$$Fe + 3HCl \rightleftharpoons FeCl_2 + 3H,$$

$$SbCl_3 + 3H = Sb + 3HCl,$$

or

$$Sb^{+++} + 3H = Sb + 3H^+.$$

(I) Filter out these flakes, and heat them with concentrated nitric acid and tartaric acid. The metal will go into solution. Nitric acid converts the metal into a trioxide(and a pentoxide).

$$2Sb + 2HNO_3 = 2NO + H_2O + Sb_2O_3$$

This trioxide dissolves in tartaric acid, forming antimony hydrogen tartrate the potassium salt of which is tartar emetic (antimony potassium tartrate).

$$Sb_2O_3 + 2[(COOH)(CHOH)_2\ COOH)],$$
$$= H_2O + 2[(COOH)(CHOH)_2\ (COO.SbO)].$$

When the antimony tartrate solution is treated with hydrogen sulphide gas, orange-red antimony sulphide is precipitated.

5. *Rhodamine B test*—This test is specific for pentavalent antimony. Since usually the solutions contain trivalent antimony, they are first oxidised as follows :—

Place a drop of the test solution on the spot plate : add some crystals of sodium nitrite and one or two drops of strong hydrochloric acid. When effervescence has ceased add a few drops of rhodamine B solution (0.01% solution). A bright red or violet colour indicates the presence of antimony.

This may also be utilised as a spot test.

Insoluble Antimony oxide, Sb_2O_4.

Fusion with sodium carbonote and sulphur—The dry insoluble antimony tetroxide is taken on a small porcelain piece and mixed with three times as much of calcined sodium carbonate and an equal quantity of sulphur (1 : 3 : 3). The whole mass is thoroughly fused. (It is better to perform the operation in a covered crucible). When the excess of sulphur has burnt and distilled off, the contents are allowed to cool. In this reaction, sodium thioantimoniate is formed.

$$2Sb_2O_4+6Na_2CO_3+23S=4Na_3SbS_4+7SO_2+6CO_2.$$

When this fused mass is acidified with an excess of dilute hydrochloric acid, hydrogen sulphide gas is evolved which can be tested either by smell or lead acetate paper (black stains), and antimonic sulphide is precipitated orange.

$$2Na_3SbS_4+6HCl=Sb_2S_5\downarrow+6NaCl+3H_2S.$$

Antimonic sulphide may also be confirmed by the reaction given in previous section.

TIN

The salts usually given are stannous chloride, stannous oxide, stannic chloride and stannic sulphate.

1. *Hydrogen sulphide* produces a brown precipitate of stannous sulphide, or yellow or yellowish-brown precipitate of stannic sulphide :

$$SnCl_2+H_2S=SnS\downarrow+2HCl,$$
$$SnCl_4+2H_2S=SnS_2\downarrow+4HCl.$$

Stannous sulphide is insoluble in *ordinary* ammonium sulphide, $(NH_4)_2S$, but it dissolves in the *yellow* ammonium sulphide, $(NH_4)_2S_x$, forming ammonium thiostannate :

$$SnS+(NH_4)_2S+S=(NH_4)_2SnS_3.$$

Stannic sulphide, however, dissolves in the ordinary ammonium sulphide forming the same thiostannate :

$$SnS_2+(NH_4)_2S=(NH_4)_2SnS_3.$$

or $$SnS_2+S^{=}=SnS_3^{=}.$$

2. Stannous salts with *mercuric chloride* give a white precipitate of calomel or mercurous chloride. For the reaction, see Mercury.

3. *Glow test*—All tin salts, and even the insoluble stannic oxide, SnO_2, when treated with zinc and strong hydrochloric acid for some time and the mixture in action is stirred with a test tube filled with water, and this test tube brought near the Bunsen flame, give bluish fluorescence at the bottom surface of the test tube. The mechanism of the reaction is not clear. The bluish fluorescence is probably due to the ignition of some hydride of tin.

This test may also be carried on a semi-micro scale.

4. A very sensitive reaction is as follows :—Prepare a borax bead, and fuse in it just a trace of copper (touch the bead with a tiny crystal of copper sulphate, and fuse). The bead will be pale blue now. Fuse now in this bead a trace of the salt suspected to contain a tin compound. A transparent bead will be obtained, the colour of which will be ruby-red when cooled.

This test is applicable to soluble and *insoluble* tin compounds.

Spot test with cacothelin—Place a drop of cocothelin solution on a drop reaction paper, and *slightly* dry up the paper. Now place a drop of stannous salt solution in the centre of the spot. The appearance of a lavender colour indicates the presence of tin. The reagent solution should be fresh.

If the salt is stannic, it should be reduced with zinc and hydrochloric acid before applying the test.

Sparingly Soluble Stannic Oxide.

Dry reaction—(*a*) Test with borax-copper bead—a ruby red bead is obtained (see above).

(*b*) Apply the glow test—Treat it with zinc and dilute sulphuric acid and see the glow on the bottom of a test tube (for details, see above).

Fusion with sodium carbonate and sulphur—The method is the same as used in the case of antimony tetroxide. Fuse the insoluble residue with a mixture of sodium carbonate and sulphur (1:3:3), on a porcelain piece (preferably in a covered crucible). When fusion is complete, and all excess sulphur burnt, take out the mass and cool it. Sodium thiostannate is formed :

$$2SnO_2 + 2Na_2CO_3 + 9S = 2Na_2SnS_3 + 2CO_2 + 3SO_2.$$

When this fused mass is acidified with dilute hydrochloric acid, hydrogen sulphide is evolved, which is tested by smell or acetate

paper, and stannic sulphide is precipitated yellow. (It is usually accompanied with a brown precipitate of stannous sulphide also).

$$Na_2SnS_3+2HCl=2NaCl+SnS_2+H_2S.$$

Stannic sulphide may further be tested in the usual way.

Chemistry of the Separation of the Second Group.

When hydrogen sulphide is passed through the solution of the given mixture in presence of dilute hydrochloric acid, the sulphides of mercury, lead, bismuth, copper, cadmium and also of arsenic, antimony and tin are precipitated according to the following typical reactions (R standing for Hg, Cu, Pb, and stannous).

$$RCl_2+H_2S=RS+2HCl.$$
$$2BiCl_3+3H_2S=Bi_2S_3+6HCl.$$
$$2AsCl_3+3H_2S=As_2S_3+6HCl.$$
$$SnCl_4+2H_2S=SnS_2+4HCl.$$

The reactions of arsenic and antimony are similar.

Use of yellow ammonium sulphide—The precipitated sulphides are digested with *yellow* ammonium sulphide. The yellow ammonium sulphide is obtained by suspending sulphur in ammonium hydroxide solution and passing hydrogen sulphide. It contains more sulphur than the ordinary ammonium sulphide, $(NH_4)_2S$, and has the general formula $(NH_4)2/S_x$. It will be seen from the following reactions, that the yellow ammonium sulphide is preferred to the ordinary sulphide in order to dissolve stannous sulphide, SnS, also which is soluble in the former one alone. Stannic sulphide dissolves in ordinary also; in both cases, the soluble complex formed is $(NH_4)_2SnS_3$.

$$SnS_2+(NH_4)_2S=(NH_4)_2SnS_3.$$
$$SnS+(NH_4)_2S_x=(NH_4)_2SnS_3+(x-2)S.$$

Arsenious sulphide dissolves in ammonium sulphide as follows: (The reactions with antimony sulphides are also similar).

$$As_2S_3+3(NH_4)_2S=2(NH_4)_3AsS_3.$$
$$As_2S_5+3(NH_4)_2S=2(NH_4)_3AsS_4.$$

These thioarsenites and thioarsenates correspond to arsenates and arsenites in which oxygen has been replaced by sulphur.

When treated with yellow ammonium sulphide, even the arsenious and antimonious compounds yield the higher compounds, thioarsenate and thioantimoniate.

The sulphides of mercury, lead, bismuth, copper and cadmium do not dissolve in ammonium sulphide. They are thus separated by filtration. They form the "Copper Group."

Arsenic Group—The filtrate consisting of the Arsenic Group is treated with dilute hydrochloric acid in excess, the thio-salts are decomposed giving back the sulphides, As_2S_5, Sb_2S_5 and SnS_2; some sulphur is also precipitated from the excess of the yellow ammonium sulphide :

$$(NH_4)_2S_x+2HCl=2NH_4Cl+H_2S+(x-1)S.$$
$$2(NH_4)_3AsS_4+6HCl=6NH_4Cl+As_2S_5+3H_2S.$$

The reactions with other thiosalts are also similar.

When the mixture of arsenic, antimony and tin (and also sulphur) is treated with strong hydrochloric acid, antimony and tin go into the solution as chlorides, but the arsenic and sulphur remain undissolved.

$$Sb_2S_5+6HCl=2SbCl_3+3H_2S+2S.$$
$$SnS_2+4HCl=SnCl_4+H_2S.$$

They are further confirmed by the tests already given. With iron and hydrochloric acid, the stannic salts are reduced to stannous, and antimony chloride is reduced to metallic antimony :

$$SbCl_3+3H=Sb+3HCl.$$
$$SnCl_4+2H=SnCl_2+2HCl.$$

Stannous chloride with mercuric chloride gives a precipitate of calomel, and finally of grey mercury :

$$SnCl_2+2HgCl_2=SnCl_4+Hg_2Cl_2.$$
$$Hg_2Cl_2+SnCl_2=SnCl_4+2Hg.$$

Antimony is dissolved in nitric acid and tartaric acid and reprecipitated as sulphide by hydrogen sulphide.

Antimony and tin may also be separated by taking advantage of the fact that the antimony sulphide can be precipitated from solutions containing oxalic acid while tin sulphide cannot be precipitated from such solutions on passing hydrogen sulphide, because of the formation of a tin complex. The mixed acidic solution of the two chlorides is made just alkaline with ammonia and a few grams of solid oxalic acid added. Tin ions form a complex, and when hydrogen sulphide is passed, it is only antimony which is precipitated as an orange sulphide. The precipitate is filtered off.

The filtrate is now made alkaline and then acidified with acetic acid. On passing hydrogen sulphide, tin is also precipitated as sulphide.

Copper Group—The precipitate left undissolved in yellow ammonium sulphide consists of

$$HgS, PbS, Bi_2S_3, CuS \text{ and } CdS.$$

When this precipitate is treated with about 33% HNO_3 all sulphides except that of mercury dissolve forming nitrates (Me=Pb, Cu or Cd).

$$8MeS+8HNO_3=3Me(NO_3)_2+2NO+4H_2O+3S.$$
$$Bi_2S_3+8HNO_3=2Bi(NO_3)_3+2NO+4H_2O+3S.$$

The residue of HgS left is dissolved in aqua regia and tested with $SnCl_2$ or copper foil, the reactions for which are given along with the First Group:

$$HgS+2HCl+O=HgCl_2+4H_2O+S.$$

Theory of Sulphide Precipitation.

The primary and secondary ionization constants for hydrogen sulphide are shown by the equations:—

$$H_2S \rightleftharpoons H^+ + HS^- \qquad \text{(i)}$$
$$HS^- \rightleftharpoons H^+ + S^- \qquad \text{(ii)}$$

$$\frac{[H^+]\times[HS^-]}{[H_2S]}=K_1=0.91\times10^{-7} \qquad \text{(i)}$$

$$\frac{[H^+]\ [S^=]}{[HS^-]}=K_2=1.2\times10^{-15}. \qquad \text{(ii)}$$

Multiplying (i) and (ii) we get

$$\frac{[H^+]^2\times[S^=]}{[H_2S]}=K_1\times K_2=1.1\times10^{-22}$$

If the solution is kept saturated with H_2S, which is the case during analysis, the concentration of H_2S is 0·1 *M*.

$$[H^+]^2\times[S^=]=[H_2S]\times1.1\times10^{-22}$$
$$=0{\cdot}1\times1{\cdot}1\times10^{-22}=1{\cdot}1\times10^{-23}$$

$$\therefore\ [S^=]=\frac{1{\cdot}1\times10^{-23}}{[H^+]^2}.$$ This is an important quantity.

Hence, if we want to vary the concentration of sulphide ions, we have got to vary $[H^+]$ in the reverse order *i.e.*, if we want to increase the sulphide ion concentration, $[S^=]$, we ought to decrease the hydrogen ion concentration, $[H^+]$, and *vice versa*.

Now in acidic solutions,(as in the Second Group), the concentration of H^+ ions is large so that the concentration of sulphide ions is very small and only those sulphides are precipitated, the solubility products of which are small. Such sulphides are HgS, CuS, Bi_2S_3, PbS, CdS, As_2S_3, Sb_2S_3, SnS, and SnS_2. Others remain in solution. The sulphides of iron, zinc, manganese, nickel and cobalt are not precipitated as their solubility products are very large and this small concentration of sulphide ions is not enough to precipitate them. CdS has an intermediate solubility product so that if there is too much of the acid, it is not precipitated. This is the reason, why it is generally precipitated after dilution.

If H_2S is passed into a neutral salt solution of Fe, Zn, Mn, Ni or Co, these metals are partially precipitated as sulphides, because the reaction is never complete as the acid liberated in the reaction ($ZnCl_2+H_2S=ZnS+2HCl$) lowers the concentration of the sulphide ions so that the product $[Me]\times[S]$ is not able to exceed the solubility products of these sulphides. Hence, the precipitation stops. If, however, H_2S is passed in solutions of these salts in presence of some alkali (say NH_4OH), the concentration of H^+ ions is considerably thrown down with the result that the concentration of the sulphide ions, $[S^{=}]$, increase so much that the product $[Me]\times[S]$ exceeds the solubility product of the sulphides of Fe, Zn, Mn, Ni or Co and they are precipitated. This is exactly what happens in the Fourth Group when the sulphides of Zn, Mn, Ni and Co are precipitated by H_2S in presence of NH_4OH.

Thus we find that sulphides, having low solubility products are precipitated in acid medium *e.g.*, HgS, PbS, CuS; sulphides having very high solubility are precipitated in the alkaline medium *e.g.*, ZnS, MnS, CoS, NiS; and the sulphides having intermediate solubility products, *e.g.*, neither too low nor too high, are precipitated in very dilute acid solutions, *e.g.*, CdS.

It is also evident that sulphides having low solubility products can be precipitated in alkaline solutions, but those having high solubility products cannot be precipitated from acid solutions.

3. Metals of the Third Group

IRON

The salts usually given are ferrous sulphate, ferrous phosphate, ferrous oxalate, ferric oxide (soluble and insoluble), ferric alum, ferric chloride and nitrate and ferric phosphate.

1. Ferrous salts are changed to ferric when heated with concentrated *nitric acid.*

$$2FeSO_4+H_2SO_4+O=Fe_2(SO_4)_3+H_2O.$$

or

$$2Fe^{++}+2H^++O=2Fe^{+++}+H_2O.$$

2. Ferric salts are reduced to ferrous, when *hydrogen sulphide gas* is passed through the solution in the Second Group; sulphur is precipitated :

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S,$$

or

$$2Fe^{+++} + S^{=} = 2Fe^{++} + S.$$

3. Ferrous salts absorb nitric oxide from nitric acid, and give brown colour of $2FeSO_4 . NO$, a reaction which is utilised in the ring test of nitrates.

$$2KNO_3 + 4H_2SO_4 + 6FeSO_4 = K_2SO_4 + 2NO + 3Fe_2(SO_4)_3 + 4H_2O.$$

$$2FeSO_4 + NO = 2FeSO_4 . NO.$$

4. *If hydrogen sulphide* is passed through a ferric or ferrous salt in *ammoniacal* solution, black precipitate of ferrous sulphide is obtained.

$$FeSO_4 + H_2S + 2NH_4OH = FeS + (NH_4)_2SO_4 + 2H_2O.$$

The precipitate is soluble in acids. A ferric salt is reduced to ferrous (equation 2), and then ferrous sulphide is precipitated.

5. A ferrous salt with *potassium ferricyanide* solution gives a deep blue colour (or precipitate] of Turnbull's blue, ferrous ferricyanide :

$$3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3[Fe(CN)_6] \downarrow + 3K_2SO_4.$$

This reaction is utilised in the titration of ferrous ammonium sulphate with potassium dichromate, in which potassium ferricyanide is used as an external indicator. Dichromate is reduced to a chromium salt.

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O. \quad [\times 3]$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3.$$

or $$Cr_2O_7^{=} + 14H^{+} + 6Fe^{++} = 2Cr^{+++} + 6Fe^{+++} + 7H_2O.$$

6. *Ammonium hydroxide* solution with ferric salt solution gives a reddish-brown precipitate of ferric hydroxide or hydrous ferric oxide.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl.$$

or $$Fe^{+++} + 3OH^{-} = Fe(OH)_3.$$

The precipitate is soluble in acids, even in dilute nitric acid. (Cf. $Mn(OH)_2$] :

$$Fe(OH)_3+3HNO_3=Fe(NO_3)_3+3H_2O.$$

The precipitate of ferric hydroxide on ignition gives ferric oxide :

$$2Fe(OH)_3=Fe_2O_3+3H_2O.$$

7. A ferric salt with *potassium ferrocyanide* solution gives a precipitate of prussian blue :

$$4FeCl_3+3K_4Fe(CN)_6=Fe\,[Fe(CN)_6]_3+12KCl.$$

8. A ferric salt with *potassium thiocyanate* gives an intense blood-red colouration of ferric thiocyanate:

$$Fe_2(SO_4)_3+6KCNS=2Fe(CNS)_3+3K_2SO_4.$$

The colour was formerly believed to be due to the formation of non-ionised $Fe(CNS)_3$ molecules but is *now* to be due to a complex ferri-thiocyanate cation, $[Fe(SCN)_6]$ which is more soluble in ether and in amyl alcohol than in water (when shaken with these solvents, the red colour passes to the organic layer).

For this reason, ferric alum is utilised as an indicator in $AgNO_3$—KCNS titrations.

9. A ferric salt with *sodium acetate* gives a reddish-brown colour, which disappears in presence of mineral acids. The test is done in neutral (test for acetate), or feebly acidic medium (see elimination of phosphates) :

$$FeCl_3+3CH_3COONa=(CH_3COO)_3Fe+3NaCl.$$

On boiling the solution, iron is precipitated as basic ferric acetate :

$$(CH_3COO)_3Fe+2H_2O=(CH_3COO).\,Fe(OH)_2+2CH_3COOH.$$

10. *Spot test with sulphosalicylic acid* :

The reagent is very sensitive, and is used as a 5% solution.

Place a drop of the reagent on the drop-reaction paper, and add a drop of the test solution. A violet colour indicates the presence of iron. This test is specific, for no other ions of Groups III and IV interfere.

CHROMIUM

The usual salts given are chrome alum, soluble (green) and insoluble (violet) chromic chloride, insoluble and soluble chromic

sulphate, insoluble chromic oxide, and potassium chromate or dichromate.

Chromates and dichromates—(*a*) Chromates are neutral to litmus while dichromates are acidic. (*b*) Solution of dichromates evolve carbon dioxide from carbonates.

Chromates when acidified with acids are converted to dichromates.

$$2K_2CrO_4+H_2SO_4=K_2Cr_2O_7+K_2SO_4+H_2O,$$
$$2CrO_4^{=}+2H^{+}=Cr_2O_7^{=}+H_2O.$$

Conversely, the dichromates are changed to chromates on addition of alkali :

$$K_2Cr_2O_7+2KOH=2K_2CrO_4+H_2O,$$

or $$Cr_2O_7^{=}+2OH^{-}=2CrO_4^{=}+H_2O.$$

Reactions

1. A solution of potassium dichromate is *reduced* to a chromium salt by (*i*) passing hydrogen sulphide through the solution; (*ii*) passing sulphur dioxide through the solution; (*iii*) adding ferrous salt to the solution, and (*iv*) adding alcohol to the solution. The potential equation is :

$$K_2Cr_2O_7=K_2O+Cr_2O_3+3O,$$

or $$K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O.$$

The reactions are utilised in ferrous sulphate titration, in the test of sulphites, and in the gravimetric estimation of chromium (ferrous sulphate is oxidised to ferric sulphate, sulphurous acid to sulphuric acid, and alcohol to aldehyde.)

2. A chromic salt solution with *ammonium hydroxide* or caustic soda solution gives a bluish or whitish green precipitate of hydrous chromic oxide.

$$CrCl_3+3NH_4OH=Cr(OH)_3\downarrow+3NH_4Cl,$$
$$CrCl_3+3NaOH=Cr(OH)_3\downarrow+3NaCl,$$

or $$Cr^{+++}+3OH^{-}=Cr(OH)_3.$$

The fresh precipitate is, however, partly soluble in an excess of a strong solution of caustic soda, forming sodium chromite:

$$Cr(OH)_3+3NaOH=Cr(ONa)_3+3H_2O.$$

The equation is reversed on boiling.

3. Chromic salt, in presence of *ammonia*, gives a precipitate of chromium hydroxide, which does not change to sulphide on passing hydrogen sulphide.

4. A chromium salt solution, when boiled with *caustic soda* and *bromine* water, is changed to a yellow chromate solution.

$$Br_2+2NaOH=NaOBr+H_2O.$$

$$2Cr(OH)_3+3NaOBr+4NaOH=2Na_2CrO_4+3NaBr+5H_2O.$$

Sodium peroxide may be used in place of bromine water.

$$2Cr(OH)_3+3Na_2O_2=2Na_2CrO_4+2H_2O+2NaOH.$$

5. A dry chromium salt, even the insoluble chromic oxide, chromic sulphate and violet chromic chloride, when fused with *sodium carbonate* and *potassium nitrate*, gives a yellow mass of sodium or potassium chromate :

$$\begin{aligned}&Cr_2O_3+3KNO_3+2Na_2CO_3\\&\quad=2Na_2CrO_4+3KNO_2+2CO_2.\end{aligned}$$

The yellow mass is soluble in acetic acid, and gives a yellow precipitate of lead chromate with lead acetate :

$$Na_2CrO_4+(CH_3COO)_2Pb=PbCrO_4+2CH_3COONa.$$

Reactions with chromates

(*a*) We have already said that a chromate solution is reduced by *hydrogen sulphide* or sulphur dioxide, in acidic solutions.

$$Cr_2O_7^{=}+14H^{+}+3S^{=}=2Cr^{+++}+7H_2O+3S.$$
$$Cr_2O_7^{=}+8H^{+}+3SO_3^{=}=2Cr^{+++}+3SO_4^{=}+4H_2O.$$

(*b*) In neutral solutions, *silver nitrate* gives a red precipitate soluble in nitric acid.

$$2Ag^{+}+CrO_4^{=}=Ag_2CrO_4\downarrow.$$

(*c*) *Lead acetate or barium chloride* gives a yellow precipitate insoluble in acetic acid, but soluble in mineral acids.

$$Ba^{++}+CrO_4^{=}=BaCrO_4\downarrow.$$

(*d*) Chromates (or dichromates) in presence of dilute sulphuric acid and *hydrogen peroxide* give blue *perchromic* acid, CrO_5, which when shaken with ether passes to the ethereal layer.

$$H_2Cr_2O_7+4H_2O_2\rightleftharpoons 2CrO_5+5H_2O$$

The test may be done on a spot-plate too.

(*e*) Prepare a one per cent solution of *diphenylamine* in strong sulphuric acid. This, when added to a chromate solution, gives intense blue colour of phenylene blue. The reaction is used in volumetric estimations.

ALUMINIUM

The usual salts given are chloride, nitrate, sulphate and potash alum. The ignited oxide, Al_2O_3, is given as insoluble.

1. A soluble aluminium salt gives with *ammonium hydroxide* a white gelatinous precipitate of aluminium hydroxide :

$$AlCl_3+NH_4OH=Al(OH)_3+3NH_4Cl,$$

or
$$Al^{+++}+3OH^-=Al(OH)_3.$$

(*a*) The precipitate is soluble in mineral acids:

$$Al(OH)_3+3HNO_3=Al(NO_3)_3+3H_2O,$$

or
$$Al(OH)_3+3H^+=Al^{+++}+3H_2O.$$

(*b*) The precipitate also dissolves in an excess of caustic soda solution, forming sodium aluminate :

$$Al(OH)_3+NaOH=NaAlO_2+2H_2O.$$

or
$$Al(OH)_3+OH^-=AlO_2^-+2H_2O.$$

The aluminate is decomposed to aluminium hydroxide when heated with a solution of ammonium chloride :

$$NaAlO_2+H_2O+NH_4Cl=Al(OH)_3+NaCl+NH_3.$$

The decomposition may be also accomplished by adding excess of nitric acid to the alkaline solution of the aluminate, heating, and finally adding ammonium hydroxide solution :

$$NaAlO_2+4HNO_3=Al(NO_3)_3+NaNO_3+2H_2O,$$
$$Al(NO_3)_3+3NH_4OH=Al(OH)_3\downarrow+3NH_4NO_3.$$

2. Test with *aluminon*—"Aluminon" is the trade name for the ammonium salt of aurin tricarboxylic acid, $C_{22}H_{14}O_9$. To a slightly acidic solution of the ammonium salt, add a few ml. of a dilute ammonium acetate and an equal volume of 0·1 per cent aqueous solution of the reagent. Make the solution ammoniacal with ammonia and ammonium carbonate solutions. A bright red precipitate is obtained.

3. *Spot test* with *alizarine* (or *alzarine-S*)—Impregnate a strip of filter paper with an alcoholic solution of alizarine (or aqueous solution of alizarine-S); and a drop of the test solution, and expose to ammonia vapours. A bright red lake will be formed.

Alizarine-S is sodium alizarine sulphonate.

Chemistry of the Separation of the Metals of the Third Group.

Use of nitric acid—The solubility product of *ferrous* hydroxide is more than that of the *ferric*, and hence, it is desirable to precipitate

iron as *ferric* hydroxide, rather than as *ferrous*. This is accomplished by oxidising ferrous salt to ferric state with nitric acid. Ferrous hydroxide, like magnesium hydroxide, is markedly soluble if the precipitation is effected by ammonium hydroxide in presence of *ammonium chloride*.

Use of ammonium chloride—Ammonium chloride prevents the precipitation of the metals of the subsequent groups in the Third Group. If ammonium chloride is not added along with ammonium hydroxide, the precipitate obtained in the Third Group is not only of the hydroxides of iron, chromium and aluminium, but may consist of the hydroxides of zinc, cobalt, and magnesium also. The function of ammonium chloride may be followed on the basis of the following considerations :—

(*a*) The solubility product of the hydroxides of the metal falls into three groups :—(*i*) hydroxides of very small solubility products, as of iron (*ic*), chromium and aluminium, (*ii*) hydroxides of moderately high solubility product,— as of zinc, ferrous, cobalt, nickel and magnesium, and (*iii*) hydroxides of high solubility product,—as of calcium, strontium and barium.

The hydroxides of the group (*iii*) (*i.e.*, calcium etc.) are not precipitated even in presence of high concentration of hydroxyl ions. The precipitation of the hydroxides of group (*ii*) can only be prevented if the hydroxyl ion concentration is markedly decreased. The hydroxyl ion concentration, as available from the dissociation of ammonium hydroxide solution is pretty high, so much so, that unless ammonium chloride is added, the solubility product of the hydroxides of group (*ii*) like magnesium is easily reached and they are precipitated. The hydroxides of iron, chromium and aluminium can be precipitated even with such concentration of hydroxyl ions, as are available from the solution of ammonia, buffered with ammonium chloride.

Ammonium hydroxide is a *weak* alkali which dissociates in the following way :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

and the degree of dissociation depends upon the following condition :

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K \text{ (a constant).} = 1{\cdot}8 \times 10^{-5}.$$

The bracketted quantities denote the corresponding concentrations. Ammonium chloride is, however, a *strong* electrolyte, being a salt of strong acid, and is almost completely dissociated as :

$$NH_4Cl \rightarrow NH_4^+ + Cl^-.$$

It is evident, therefore, that if ammonium chloride is added to ammonium hydroxide solution, the ammonium ion concentration is markedly increased. Now we have to maintain a constant value of K, the dissociation constant, and this can only happen when the concentration of OH-ions is correspondingly decreased. Thus the addition of ammonium chloride decreases the hydroxyl ion concentration of ammonium hydroxide to such an extent that the hydroxides of magnesium, zinc etc., are not precipitated. The decreased hydroxyl ion concentration is still sufficient to precipitate the hydroxides of iron, chromium and aluminium.

Example—What would be the fall in OH-ion concentration of ammonia solution ($0{\cdot}1\,M$) on adding $0{\cdot}5$ gram-mol. ($26{\cdot}75$g.) of ammonium chloride to one litre of the solution?

Dissociation constant of ammonia is $1{\cdot}8 \times 10^{-5}$,

$$\frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} = 1{\cdot}8 \times 10^{-5}$$

In $0{\cdot}1\,M$ ammonia solution let the concentration $[NH_4^+]$ $=[OH^-]$ be aqual to $\frac{a}{10}$, and $[NH_4OH]=\frac{1-a}{10}$, since $v=10$ liters.

Then

$$[NH_4^+]\,[OH^-] = 1{\cdot}8 \times 10^{-5} \times [NH_4OH]$$

$$\frac{a}{10} \times \frac{a}{10} = 1{\cdot}8 \times 10^{-5}\,\frac{(1-a)}{10}$$

$$\frac{a^2}{100} = \frac{1{\cdot}8 \times 10^{-5}(1-a)}{10}$$

$$a = \sqrt{(1{\cdot}8 \times 10^{-5} \times 10)} = 0{\cdot}0134$$

$(1-a)$ is very nearly equal to 1, since a is very small,

$\therefore \qquad a = 0{\cdot}0134$

$\therefore \quad [NH_4^+]=[OH^-]=0{\cdot}00134$, and $[NH_4OH]=\frac{1-0{\cdot}0134}{10}$ $=0{\cdot}09866$

when $0{\cdot}5M$- ammonium chloride is added, which being a strong electrolyte is completely ionized, ammonium ions are almost all derived from it, and $[NH_4^+]=0{\cdot}5$, and almost the whole of NH_4OH is undissociated, i.e. $[NH_4OH]=0{\cdot}1$. Let the concentration of new OH^- be $a'/10$, then

$$\frac{[NH_4^+]\,[OH^-]}{NH_4OH]}=\frac{O\cdot^5\times\alpha'/10}{0\cdot1}=1\cdot8\times10^{-5}$$

whence $\alpha'=3\cdot6\times10^{-5}$

and $[OH^-]=3\cdot6\times10^{-5}$. Thus the concentration of OH^-ions has fallen from 0·00134 to 0·0000036.

(*b*) With some of the metals, ammonium chloride forms such soluble complex salts from which the metal is not precipitated as hydroxide, *e.g.*, $Ni(NH_3)_6Cl_2$ and $Ni(NH_3)_9\ Cl_2$, or $Mg\ (NH_4)Cl_3$ and $Zn(NH_4)Cl_3$.

(*c*) Ammonium chloride is useful in another respect also. Being a strong electrolyte, it readily coagulates the colloidal hydroxides of chromium and aluminium, which have otherwise a marked tendency to pass into the colloidal form.

Interfering acids—There are certain acid radicals which interfere in the proper group separation of the analysis. These acid radicals are oxalate, fluoride phosphate and also borate. These acid radicals interfere in the sense that when they are present, the precipitate appearing in the Third Group does not necessarily consist of hydroxide (or oxalate, phosphate etc.) of the members of the Third Group only, but may consist of the oxalates, fluorides or phosphates of the members of the subsequent groups, as zinc, calcium, magnesium, etc. The latter are also precipitated, as soon as the solution becomes alkaline on the addition of ammonia. Whenever such interfering acid radicals are present, they ought to be eliminated first before proceeding for the regular group analysis. These acids do not interfere, so long as the medium is acidic (*i.e.*, up to the Second Group).

Elimination of oxalates or any other organic matter—It is not necessary to remove the organic matter until after the precipitation of the Second Group. Large quantities of tartaric and oxalic acids interfere, however, with the precipitation of tin. If tin is present, one ought so remove these acids before passing hydrogen sulphide. The organic matter is removed if the solution is evaporated to dryness and strongly ignited on a porcelain piece. The organic matter chars, and the oxalates (which do not char) are converted into oxides and carbonates :

$$CaC_2O_4=CaCO_3+CO,$$
$$CaCO_3=CaO+CO_2.$$

The oxalates are also oxidised when they are treated in solution with aqua regia or a mixture of concentrated hydrochloric acid and potassium chlorate :

$$CaC_2O_4+2HCl+O=CaCl_2+H_2O+2CO_2.$$

It should be remembered that salts of mercury, arsenic or antimony are volatile and if they are present, the mixture cannot be subjected to ignition unless they are removed.

In such cases, the entire precipitate of the Third Group is taken and ignited, or the oxalates in the original mixture are oxidised by concentrated hydrochloric acid and potassium chlorate over a water bath. A quantity of about 1 gram of chlorate would be necessary, which is added in lots every five minutes.

Elimination of fluorides and borates—The fluorides and borates are eliminated either in the original mixture or in the precipitate appearing in the Third Group. The mixture is evaporated to dryness along with concentrated hydrochloric acid. The more volatile hydrofluoric acid is thus displaced :

$$CaF_2+2HCl=CaCl_2+H_2F_2.$$

On repeating the process a number of times, boric acid is also *volatilised* along with *steam*, slowly but completely;

$$Ca(BO_2)_2+2HCl=CaCl_2+2HBO_2.$$
$$2HBO_2=B_2O_3+H_2O.$$

Elimination of phosphates—So long as the medium is acidic, all the phosphates remain in solution, but when it becomes alkaline on the addition of ammonia, as in the Third Group, not only the phosphates of the Iron Group but also of the subsequent groups are precipitated. It is not necessary that they were given as phosphates in the initial mixture. A mixture originally consisting of sodium phosphate, Na_2HPO_4, and a calcium salt, would also precipitate out as calcium phosphate in the Iron Group.

$$Na_2HPO_4+CaCl_2=CaHPO_4\downarrow+2NaCl.$$

There are three groups of phosphates, (*i*) one with very high solubility products as sodium or ammonium phosphate; they are not precipitated in any medium; (*ii*) one with moderately high solubility products as of zinc and calcium; they are precipitated only in alkaline medium; (*iii*) one with fairly small solubility product as of iron, aluminium and chromium which are precipitated not only in alkaline medium, but also in feebly acidic medium (the buffered medium of sodium acetate and acetic acid).

It can easily be shown on the basis of ionic theory, that much less phosphate ions are available from phosphoric acid, if the medium is acidic, and more phosphate ions are available as the acidity decreases. The acid has the first stage ionisation as follows :—

$$H_3PO_4\rightleftharpoons H^++H_2PO_4^-$$

for which $$\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}=K\text{ (a constant)}=7{\cdot}52\times10^{-3}$$

The condition specifies, that as the concentration of H^+ increases, the concentration of $H_2PO_4^-$ would fall down and *vice versa.* Thus :

(*i*) if the medium is highly acidic (as in presence of HCl)—very few phosphate ions are available, —no phosphates are precipitated.

(*ii*) if the medium is fairly acidic (as in presence of acetic acid alone)—relatively more phosphate ions are available, yet insufficient to precipitate the phosphates of the Iron Group.

(*iii*) if the medium is of buffered sodium acetate and acetic acid, more phosphate ions are available quite sufficient to precipitate the phosphates of the Iron Group, but still insufficient to precipitate the phosphates of the subsequent groups.

(*iv*) if the medium is ammoniacal—much more phosphate ions are available, quite sufficient to precipitate the phosphates of Zinc, Calcium and Magnesium Groups.

From this it would be clear that if we choose a buffered medium of sodium acetate and acetic acid, the phosphates of the members of Zinc and subsequent Groups would be held in solution, but for the analysis of these groups, the medium has to be again made ammoniacal, and therefore, it is necessary to eliminate phosphates by a suitable method. This method consists of addition of ferric chloride solution in the buffered solution of sodium acetate and acetic acid. As ferric phosphate is insoluble in this medium, ferric ions from ferric chloride would combine with almost all the phosphate ions of the solution, and come down as a precipitate. Ferric chloride has to be added to the requisite extent only, because the excess of ferric chloride peptises the ferric phosphate precipitate, which again passes to the colloidal state.

How sodium acetate decreases the acidity of acetic acid is seen from the following considerations :—

Acetic acid, a weak acid, dissociates in the solution as follows :

$$CH_3COOH = CH_3COO^- + H^+,$$

$$\frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} = K \text{ (a constant)} = 1{\cdot}82 \times 10^{-5}$$

Sodium acetate is a strong electrolyte, which almost completely ionises as :

$$CH_3COONa = Na^+ + CH_3COO^-.$$

When a mixture of the two is taken, acetate ions are considerably increased, with the result, that to maintain the value of K as constant, the number of H^+ ions decreases. Less the hydrogen ions in a medium, the less is the acidity.

Sodium acetate helps in another way also; it indicates the extent to which ferric chloride has to be added. With a free ferric ion it gives brownish-red colour. When the mixture assumes the colour of the prepared tea, the adition of ferric chloride has to be stopped.

Example. 0·1 gram. mol. (8·20 grams) of anhydrous sodium acetate has been added to, 1 litre of 0·1 mol. acetic acid. Calculate the fall of degree of ionisation of acetic acid.

$$K=\frac{[CH_3COO^-][H^+]}{[CH_3COOH]}=\frac{\alpha^2}{(1-\alpha)v}=\frac{\alpha^2}{v}=1{\cdot}8=\times 10^{-5}$$

(if α is small compared to unity).

For 0·1 mol. of acetic acid, $v=10$

$$\therefore \qquad \frac{\alpha^2}{10}=1{\cdot}82\times 10^{-5}$$

whence $\qquad \alpha=\sqrt{(1{\cdot}82\times 10^{-5}\times 10)}=0{\cdot}0135$

Thus in 0·1 mol. acetic acid, $[H^+]=[CH_3COO^-]=0{\cdot}0135$ and $[CH_3COOH]=1-0{\cdot}0135=0{\cdot}0986$.

When 0·1 gram. mol. sodium acetate has been added which is a strong electrolyte and is completely ionised, acetate ion concertration is 0·1 gram-mol. In presence of Na-acetate, acetic acid is ionised to a small extent only. Let it be ionised to α' extent.

$$[CH_3COO^-]=0{\cdot}1; \quad [CH_3COOH]=0{\cdot}1$$

$$\therefore \quad \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}=\frac{0{\cdot}1\times[H^+]}{0{\cdot}1}=\frac{0{\cdot}1\times 0{\cdot}1\alpha'}{0{\cdot}1}=1{\cdot}82\times 10^{-5}$$

whence $\quad \alpha'=1{\cdot}82\times 10^{-4}$

$$\therefore \quad [H^+]=\frac{\alpha'}{v}=\frac{1{\cdot}82\times 10^{-4}}{10}=1{\cdot}82\times 10^{-5}$$

Thus the value of α has fallen from 0·0135 (or 1·35%) to $1{\cdot}82\times 10^{-4}$ (or 0·0182%). The H^+ ion concentration has fallen from 0·0135 to 0·0000182.

Treatment of the mixed precipitates of the Third Group after eliminating interfering acids—The precipitates consist of the hydroxides (or even phosphates) of iron, chromium and aluminium. The mixed precipitates are treated with caustic soda and bromine water or

caustic soda and sodium peroxide, the potential oxidation reactions are :

$$NaOH + Br_2 = NaOBr + HBr = NaBr + HBr + O.$$
$$Na_2O_2 + H_2O = 2NaOH + O.$$

The available oxygen oxidises chromium hydroxide to yellow soluble sodium chromate :

$$2Cr\,(OH)_3 + 4NaOH + 3O = 2Na_2CrO_4 + 5H_2O.$$

or $$2Cr\,(OH)_3 + 4OH^- + 3O = 2CrO_4^{=} + 5H_2O.$$

The caustic alkali simultaneously converts aluminium hydroxide to sodium aluminate :

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O.$$

If chromium be absent, only caustic soda would do for aluminium, and no bromine water has to be added.

Chromium and aluminium, forming soluble chromate and aluminate, pass into the filtrate, and the residue contains the hydrous oxides of manganese and iron. When treated with dilute nitric acid, iron oxide dissolves, forming ferric nitrate but the manganese oxide remains as the insoluble residue :

$$Fe(OH)_3 + 3HNO_3 = Fe(NO_3)_3 + 3H_2O.$$

Iron is tested by potassium ferrocyanide test, and manganese by the manganate test (fusion with KNO_3 and sodium carbonate).

$$Mn(OH)_2 + Na_2CO_3 + 2O = Na_2MnO_4 + CO_2 + H_2O.$$

or

$$MnSO_4 + 2KNO_3 + 2Na_2CO_3$$
$$= Na_2MnO_4 + 2KNO_2 + Na_2SO_4 + 2CO_2.$$

The green mass, when dissolved in an acid, gives a pink colour of sodium permanganate:

$$3Na_2MnO_4 + 4HCl = 2NaMnO_4 + MnO(OH)_2 \downarrow$$
$$+ 4NaCl + H_2O.$$

Sodium aluminate breaks up to aluminium hydroxide when heated with ammonium chloride (or with nitric acid and then ammonia solution) and chromate is tested with lead acetate, after thoroughly acidifying with acetic acid. The reactions have already been given.

4. Metals of the Fourth Group

ZINC

The substances usually given are zinc sulphate, chloride, phosphate, carbonate, nitrate, bromide and oxide.

1. A zinc salt solution, when treated with *ammonium hydroxide*, gives a precipitate of zinc hydroxide, but the precipitate is soluble in presence of ammonium chloride:

$$ZnCl_2+2NH_4OH \rightleftharpoons Zn(OH)_2\downarrow+2NH_4Cl.$$

or

$$Zn^{++}+2OH^-=Zn(OH)_2\downarrow.$$

2. A zinc salt gives a precipitate of zinc carbonate, basic carbonate, or hydroxide, when treated with sodium carbonate solution. The precipitate is soluble in an excess of the alkali solution.

$$ZnCl_2+Na_2CO_3=ZnCO_3+2NaCl.$$

3. The precipitate of zinc hydroxide dissolves in *caustic alkali* solution, forming sodium zincate:

$$Zn(OH)_2+2NaOH=Zn(ONa)_2+2H_2O,$$
$$Zn(OH)_2+2OH^-=ZnO_2^{=}+2H_2O.$$

4. When *hydrogen sulphide* is passed through a soluble zinc salt in neutral or alkaline medium, and even through sodium zincate, a white precipitate of zinc sulphide is formed.

The precipitate is soluble in mineral acids, but *not* in acetic acid (cf. MnS).

$$ZnCl_2+(NH_4)_2S=ZnS\downarrow+2NH_4Cl,$$
$$Zn^{++}+S^{=}=ZnS\downarrow.$$
$$Zn(ONa)_2+H_2S=ZnS\downarrow+2NaOH.$$

5. The precipitates of zinc hydroxide or carbonate when ignited strongly, leave zinc oxide, which assumes yellow tint while hot, but white when cold.

$$ZnCO_3=ZnO+CO_2,$$
$$Zn(OH)_2=ZnO+H_2O.$$

The reaction is utilized in gravimetric estimation of zinc as oxide.

Zinc oxide is readily reduced to metallic zinc by the carbon of the filter paper during incineration :

$$ZnO+C=Zn+CO.$$

The metal zinc is volatile at the temperature of the Bunsen flame. To prevent the loss thus incurred, the filter paper is soaked with a strong solution of ammonium nitrate, which acts as an oxidising agent:

$$NH_4NO_3 + C = N_2 + CO + 2H_2O.$$

6. *Rinmann's green test*—Saturate a piece of filter paper with the solution of zinc salt and a very small amount of cobalt nitrate solution. Wrap the filter paper around a platium wire (or place it in a crucible), and incinerate it until nothing but a light ash remains. If the ash is coloured bright green, zinc is indicated. Cobalt zincate, $CoZnO_2$, is formed in the reaction.

7. *Orange* IV *spot test*—To a drop of Orange IV acidified with a drop of dilute sulphuric acid (1:24) in a test tube, add 3-5 drops of a 2 per cent solution of $K_3Fe(CN)_6$. A red colour is produced. Now add a drop of the zinc solution. A green coloration indicates the presence of zinc.

MANGANESE

The salts usually given are managanous chloride, sulphate, nitrate, carbonate, oxalate and phosphate and also the oxides, and permanganate. The permanganates are reduced to a manganese salt when hydrogen sulphide is passed through the solution in the Second Group.

$$2KMnO_4 + 5H_2S + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S,$$

or $$2MnO_4^- + 16H^+ + 5S^= = 2Mn^{++} + 8H_2O + 5S.$$

1. A managanese compound, whether oxide or a salt when fused with *sodium carbonate* and *potassium nitrate* (or chlorate) in the oxidising flame gives a deep green mass of sodium manganate:

$$MnO_2 + Na_2CO_3 + O = Na_2MnO_4 + CO_2.$$

This mass when acidified with dilute sulphuric acid, gives a rose-red coloration on account of the formation of permanganate:

$$3Na_2MnO_4 + 2H_2SO_4 = 2NaMnO_4 + MnO(OH)_2 + 2Na_2SO_4 + H_2O.$$

2. A managanese salt in ammoniacal solution gives a flesh coloured precipitate of manganous sulphide when treated with *hydrogen sulphide* :

$$MnCl_2 + (NH_4)_2S = MnS \downarrow + 2NH_4Cl.$$

or $$Mn^{++} + S^= = MnS \downarrow.$$

The precipitate is soluble in acetic acid (cf. zinc) and mineral acids.

3. A manganese salt gives a white precipitate of manganous hydroxide with *ammonium hydroxide*, but the precipitate dissolves in ammonium chloride; yet it may coprecipitate with hydrous iron oxide.

$$MnCl_2+2NH_4OH=Mn(OH)_2\downarrow+2NH_4Cl.$$

The precipitate turns brown on exposure to air, owing to the formation of manganic hydroxide, $MnO\,(OH)_2$:

$$Mn(OH)_2+O=MnO(OH)_2.$$

4. *Sodium bismuthate test*—Place a drop of the solution on the spot plate. Add a drop of strong nitric acid, and then some solid sodium bismuthate, $NaBiO_3$. The purple colour of permanganate ion appears:

$$5BiO_3^-+14H^++2Mn^{++}=2MnO_4^-+5Bi^{+++}+7H_2O.$$

5. When a manganese salt, solid or solution, is heated with concentrated nitric acid and some crystals of potassium chlorate, a dark brown precipitate of MnO_2 is obtained. This is a very sensitive test for Mn and is specific, but must be performed in complete absence of Cl ions.

$$MnO+O=MnO_2\downarrow.$$

Under these conditions, no other metal gives this test.

6. *Benzidine test*—Take a drop of the test solution on a drop-reaction paper. Now add a drop of strong caustic soda solution. When the drop has stopped spreading, a drop of tartaric acid solution and then one drop of benzidine soloution are added. A blue colour indicates manganese.

COBALT

The usual salts given are sulphate, chloride, nitrate, carbonate and oxides. The anhydrous salts, and their solutions in concentrated hydrochloric acid, are blue (or green), but the blue solution on dilution becomes red or pink. The anhydrous cobalt sulphate is, however, red.

1. In ammonium hydroxide solution, a cobalt salt gives a black precipitate of sulphide when *hydrogen sulphide is* passed through

$$CoCl_2+(NH_4)_2S=CoS\downarrow+2NH_4Cl,$$

or $$Co^{++}+S^{=}=CoS.$$

The fresh precipitate is slightly soluble in dilute acids, but after some time, it is rendered completely insoluble. But it is

readily soluble in aqua regia or a mixture of hydrocholoric acid and potassium chlorate.

$$CoS + 2HCl + O = CoCl_2 + H_2O + S.$$

2. With *potassium cyanide*, a buff-coloured precipitate of cobaltous cyanide is obtained, which dissolves in an excess of the reagent, forming the complex *cobaltocyanide* :

$$CoCl_2 + 2KCN = Co(CN)_2 + 2KCl$$
$$Co(CN)_2 + 4KCN = K_4Co(CN)_6.$$

This is easily oxidised to potassium cobalticyanide even on boiling with water alone (more rapidly in presence of acids):

$$2K_4Co(CN)_6 + O + H_2O = 2K_3Co(CN)_6 + 2KOH.$$

Cobalt ion is not precipitated from this very stable complex by any of the usual reagents. Caustic soda and bromine water have no action.

3. Cobalt salts in neutral solutions, acidified with acetic acid, produce brilliant yellow precipitate with *potassium nitrite* solution; at first the cobalto-nitrite complex is formed which is then oxidised to cobaltinitrite (HNO_2 acts as an oxidising agent: $2OH.NO = 2NO + H_2O + O$) :

$$CoCl_2 + 6KNO_2 = K_4Co(NO_2)_6 + 2KCl.$$
$$2K_4Co(NO_2)_6 + 2CH_3COOH + O$$
$$= 2K_3Co(NO_2)_6 + 2CH_3COOK + H_2O.$$

4. A cobalt salt gives with an excess of *sodium bicarbonate* a precipitate of cobalt carbonate, which further forms a soluble complex, sodium *cobalto-carbonate*:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2,$$
$$Na_2CO_3 + CoCl_2 = CoCO_3 + 2NaCl,$$
$$CoCO_3 + 2Na_2CO_3 = Na_4Co(CO_3)_3.$$

The reactions may also be represented as follows:—

$$CoCl_2 + 2NaHCO_3 = Co(HCO_3)_2 + 2NaCl$$
$$Co(HCO_3)_2 + 4NaHCO_3 = Na_4Co(CO_3)_3 + 3H_2O + 3CO_2$$
$$CoCl_2 + 6NaHCO_3 = Na_4Co(CO_3)_3 + 2NaCl + 3H_2O + 3CO_2$$

This is oxidised in presence of an oxidising agent like bromine water to sodium *cobalti-carbonate* :

$$2Na_4Co(CO_3)_3 + 2NaHCO_3 + O$$
$$= 2Na_3Co(CO_3)_3 + 2Na_2CO_3 + H_2O.$$

This complex is very stable and has an apple green colour which remains unchanged on heating. Cobalt ion is not precipitated from this complex by the usual reactions (cf. nickel, Palit's test).

5. *a-Nitroso-β-Naphthol test*—To a drop of cobalt test solution on the white spot plate, add a drop of a solution of the reagent. A brownish-red precipitate indicates cobalt.

6. *Borax bead test*—The bead is blue.

7. *Vogel's test with ammonium thiocyanate*—The reagent gives beautiful blue double thiocyanate, $(NH_4)_2Co(SCN)_4$. Place a drop of cobalt test solution on a spot plate, and add to it 3 drops of alcohol, or better, acetone. Drop in a crystal of ammonium thiocyanate. A blue colour (which on dilution becomes pink) is obtained if cobalt is present. The test is performed after removing iron (ferrous iron does not interfere with the test).

NICKEL

The salts usually given are nickelous sulphate, carbonate, chloride, nitrate and phosphate. The solutions are usually green but when mixed in certain proportions, render the pink of a cobalt solution colourless.

1. In ammoniacal solution, on passing *hydrogen sulphide*, nickel salts give a black precipitate of nickel sulphide.

$$NiCl_2+(NH_4)_2S=NiS\downarrow+2NH_4Cl,$$
$$Ni^{++}+S^{=}=NiS.$$

The precipitate, when fresh, is slightly soluble in dilute acids and more so in concentrated acids and very readily in a mixture of concentrated hydrochloric acid and potassium chlorate:

$$NiS+2HCl+O=NiCl_2+H_2O+S.$$

2. Nickel salts in alkaline solutions give a precipitate of nickelous hydroxide. The precipitate is soluble in an excess of *ammonia* solution, and also in acids:

$$NiCl_2+2NaOH=Ni\ (OH)_2\downarrow+2NaCl.$$
$$Ni(OH)_2+2NH_4Cl+4NH_4OH=[Ni(NH_3)_6]\ Cl_2+6H_2O$$

This is why no precipitate of nickel hydroxide is formed in presence of ammonium chloride in the Iron Group.

3. With *potassium cyanide*, nickel produces a green precipitate of nickelous cyanide, which dissolves in an excess of the reagent forming a double cyanide:

$$NiCl_2+2KCN=Ni\ (CN)_2+2KCl.$$
$$Ni\ (CN)_2+2KCN=K_2Ni\ (CN)_4 \text{ or } 2KCN.\ Ni\ (CN)_2.$$

This is not a stable complex in the sense that it has a high second dissociation constant and dissociates appreciably as:

$$K_2Ni\ (CN)_4 \rightleftharpoons 2K^+ + Ni\ (CN)_4^{--}$$
$$Ni\ (CN)_4^{--} \rightleftharpoons Ni^{++} + 4(CN)^-.$$

From this solution, nickel cyanide is, therefore, precipitated on adding acid. The complex is easily decomposed by bromine water in presence of alkali; a black oxide of nickel is obtained:

$$Br_2 + 2NaOH = 2NaBr + H_2O + O.$$
$$2K_2Ni\ (CN)_4 + O + 4KOH = Ni_2O_3 + 8KCN + 2H_2O.$$

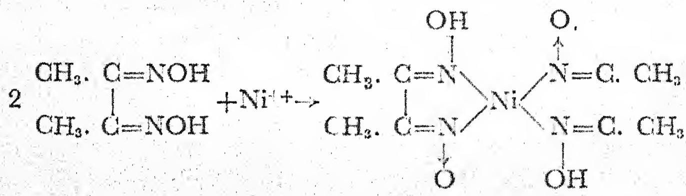
The reaction is utilised in the separation of nickel from cobalt.

4. Nickel does not form the complex carbonates with sodium bicarbonate, and on heating in an alkaline medium with bromine water, are oxidised to black oxide of nickel:

$$NiCl_2 + 2NaHCO_3 = NiCO_3 + 2NaCl + H_2O + CO_2,$$
$$2NiCO_3 + 4NaOH + O = Ni_2O_3 + 2Na_2CO_3 + 2H_2O.$$

The reaction is utilised in separation of nickel from cobalt.

Dimethyl glyoxime test—One per cent. alcoholic solution of the reagent should be used. The reagent is :



The reagent with nickel salt gives a voluminous carmine precipitate, insoluble in water, ammonia or acetic acid, but soluble in mineral acids.

The reagent with nickel salt gives a voluminous carmine precipitate, insoluble in water, ammonia or acetic acid, but soluble in mineral acids.

The reaction can be utilised as a spot test for nickel also.

Chemistry of the separation of the metals of the Fourth Group

Zinc and manganese separation—The precipitate obtained by passing hydrogen sulphide in the ammoniacal solution consists of the sulphides of zinc, manganese, cobalt and nickel. The precipitate is allowed to age for some minutes, and then treated with dilute hydrochloric acid. The sulphides of zinc and manganese thus dissolve:

$$ZnS + 2HCl = ZnCl_2 + H_2S.$$
$$MnS + 2HCl = MnCl_2 + HS.$$

Cobalt and nickel sulphides are separated at this stage by filtration. From the filtrate, hydrogen sulphide is driven off by boiling and the filtrate treated with caustic soda. With an excess of this reagent, zinc goes into the solution forming sodium zincate, whereas, manganese gives a residue of hydrous manganese oxide:

$$ZnCl_2 + 2NaOH = Zn(OH)_2 + 2NaCl.$$
$$Zn(OH)_2 + 2NaOH = \underset{\substack{\uparrow \\ \textit{soluble}}}{Zn(ONa)_2} + 2H_2O.$$

$$MnCl_2 + 2NaOH = \underset{\substack{\uparrow \\ \textit{insoluble}}}{Mn(OH)_2} + 2NaCl.$$

Manganese oxide is filtered off and confirmed by the bead test or fusion with KNO_3 and Na_2CO_3 or with concentrated HNO_3 and $KClO_3$. Zinc in the filtrate is tested by passing hydrogen sulphide:

$$Zn(ONa)_2 + H_2S \rightarrow ZnS \downarrow + 2NaOH.$$

On the basis of above reactions, a separation of cabalt and nickel may easily be effected. As the bead reaction of cobalt is is very characteristic, unmasked by the presence of nickel, the problem is only to identify nickel in presence of cobalt. To the mixture of the two, an excess of potassium cyanide is added. Cobalt forms a complex salt, potassium cobalto-cyanide, which in slightly acid solutions on exposure to air, is converted to another stable complex, potassium cobalticyanide, $K_3Co(CN)_6$. This complex remains unchanged when heated further even in an alkaline medium.

In acid medium, nickel forms only nickel cyanide with KCN and no complex. In alkaline solutions also, it gives readily oxidisable double salt, $Ni(CN)_2, 2KCN$. So when it is boiled with NaOH and bromine water or by a solution of sodium hypochlorite, the black oxide of nickel is precipitated. This gives an identification of nickel. It may be filtered off, and the solution dried, ignited and fused with borax to give a test for cobalt.

COBALTI-NITRITE TEST—Cobalt is also readily identified by this test. When a cobaltous salt acidified with acetic acid is treated with potassium nitrite solution, it gives a yellow precipitate of complex potassium cobalti-nitrite.

$$CoCl_2 + 5KNO_2 + 2HNO_2 = K_3Co(NO_2)_6 \downarrow + 2KCl + NO + H_2O.$$

Nickel does not give such a complex; thus cobalt is precipitated and then nickel tested in the filtrate.

PALIT'S TEST WITH BICARBONATE—Another qualitative identification of cobalt and nickel in presence of each other is based on the fact that cobalt salts form a soluble pink complex with sodium bicarbonate similar to potassium cobalto-cyanide:

$$CoCl_2+2NaHCO_3=Co(HCO_3)_2+2NaCl,$$
$$4NaHCO_3+Co\ (HCO_3)_2=Na_4Co(CO_3)_3+3H_2O+3CO_2$$

This sodium cobalto-carbonate is oxidised in presence of oxidising agents like bromine water forming sodium cobalti-carbonate, $Na_3Co(CO_3)_3$, which is apple-green in colour and is very stable and does not change on heating too. On the other hand, nickel does not form complex carbonates and on heating in an alkaline medium with bromine water, is oxidised to black nickelic oxide.

To perform the test, thus an excess of sodium bicarbonate is added to the chlorides of nickel and cobalt (obtained by dissolving their sulphides in concentrated HCl in presence of one crystal of potassium chlorate and removing the excess of HCl by evaporation), till the cobalt settles down as a pinkish powder, and then bromine added. In presence of cobalt, an apple-green colour will be obtained in *cold*. Now, the mixture is heated, and if a black colour with a black deposit on the sides of the test tube appears, then nickel is also confirmed.

Metals of the Fifth Group

BARIUM

The usual salts given are barium carbonate, chloride, nitrate, phosphate, and the insoluble sulphate.

1. The insoluble barium sulphate is decomposed when heated with sodium carbonate solution in excess.

$$Na_2CO_3+BaSO_4\rightleftharpoons BaCO_3+Na_2SO_4.$$

Barium carbonate is then dissolved in acid, giving a soluble barium salt.

2. When to the ammoniacal solution of a barium salt is added *ammonium carbonate* solution, a white precipitate of barium carbonate is obtained which is soluble in acetic acid :

$$BaCl_2+(NH_4)_2CO_3=BaCO_3\downarrow+2NH_4Cl,$$
or
$$Ba^{++}+CO_3^{=}=BaCO_3$$
$$BaCO_3+2CH_3COOH=(CH_3COO)_2Ba+H_2O+CO_2.$$

The barium acetate solution with *potassium chromate* gives a yellow precipitate of barium chromate :

$$(CH_3COO)_2Ba+K_2CrO_4=BaCrO_4\downarrow+2CH_3COOK,$$

or,

$$Ba^{++}+CrO_4^{=}=BaCrO_4.$$

The precipitate is soluble in mineral acids but insoluble in acetic acid.

3. Barium sulphate is reduced by *carbon* to barium *sulphide* when heated together strongly :

$$BaSO_4+4C=BaS+4CO.$$

4. A soluble barium salt gives a precipitate of barium sulphate with a soluble sulphate or sulphuric acid; the precipitate is insoluble in acids :

$$BaCl_2+H_2SO_4=BaSO_4\downarrow+2HCl.$$

STRONTIUM

The salts usually given are carbonate, chloride, nitrate, phosphate and the insoluble strontium sulphate.

1. In ammoniacal solution, *ammonium carbonate* gives a precipitate of strontium carbonate with a strontium salt :

$$SrCl_2+(NH_4)_2CO_3=SrCO_3\downarrow+2NH_4Cl.$$

or

$$Sr^{++}+CO_3^{=}=SrCO_3$$

The precipitate is soluble in acetic acid :

$$SrCO_3+2CH_3COOH=(CH_3COO)_2Sr+H_2O+CO_2.$$

From the strontium acetate solution, strontium chromate is not precipitated on the addition of potassium chromate in presence of acetic acid.

2. On the addition of *ammonium sulphate* (calcium sulphate or dilute sulphuric acid even), a precipitate of strontium sulphate appears slowly though completely. Scratching of the sides of the beaker from inside may be necessary.

$$(CH_3COO)_2Sr+(NH_4)_2SO_4=SrSO_4\downarrow+2CH_3COONH_4.$$

3. *Ammonium oxalate* with a soluble strontium salt gives a white precipitate of strontium oxalate, insoluble in acetic acid.

$$SrCl_2+(NH_4)_2C_2O_4=SrC_2O_4\downarrow+2NH_4Cl.$$

CALCIUM

The samples usually given are carbonate, chloride, phosphate, oxalate, nitrate and oxide.

1. A soluble salt in ammoniacal or neutral solution gives a precipitate of calcium carbonate with *ammonium carbonate* :

$$CaCl_2 + (NH_4)_2CO_3 = 2NH_4Cl + CaCO_3 \downarrow ,$$

or,

$$Ca^{++} + CO_3^{--} = CaCO_3 \downarrow .$$

The precipitate is soluble in acetic acid, and from this solution no precipitate appears on the addition of potassium chromate or ammonium sulphate. With the latter reagent, it forms a soluble double salt $CaSO_4.(NH_4)_2SO_4.H_2O$.

2. With *ammonium oxalate*, it forms calcium oxalate, insoluble in acetic acid :

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 \downarrow + 2NH_4Cl.$$

The oxalate is soluble in mineral acids.

Chemistry of the separation of the metals of the Fifth Group.

On the addition of ammonium carbonate to the filtrate of the Fourth Group, the metals of the Fifth Group are precipitated as carbonates : (M stands for Ca, Sr, and Ba).

$$MCl_2 + (NH_4)_2CO_3 = MCO_3 \downarrow + 2NH_4Cl.$$

All the three carbonates are soluble in acetic acid :

$$MCO_3 \downarrow + 2CH_3COOH = (CH_3COO)_2M + H_2O + CO_2.$$

When potassium chromate is added to the solution, barium chromate is precipitated which is filtered off :

$$(CH_3COO)_2Ba + K_2CrO_4 = BaCrO_4 \downarrow + 2CH_3COOK.$$

To the filtrate is added ammonium sulphate, which slowly precipitates strontium sulphate :

$$(CH_3COO)_2Sr + (NH_4)_2SO_4 = SrSO_4 \downarrow + 2CH_3COONH_4.$$

Strontium sulphate is removed by filtration, and ammonium oxalate added to the filtrate. Calcium oxalate is precipitated :

$$(CH_3COO)_2Ca + (NH_4)_2C_2O_4 = CaC_2O_4 \downarrow + 2CH_3COONH_4.$$

6. Metals of the Sixth Group.

MAGNESIUM

The salts usually given are its chloride, sulphate, carbonate, bromide, and phosphate, and also its oxide.

1. With ammonia solution, but in absence of ammonium chloride, magnesium salts give a white precipitate of magnesium hydroxide :

$$MgCl_2+2NH_4OH=Mg(OH)_2\downarrow+2NH_4Cl.$$

The precipitate is, however, soluble in presence of an excess of ammonium chloride.

2. If magnesium be present, the ammonium chloride-ammonium hydroxide medium gives a crystalline precipitate of magnesium ammonium phosphate with *sodium phosphate* :

$$MgCl_2+Na_2HPO_4+NH_4OH=Mg(NH_4)PO_4+2NaCl+H_2O.$$

The precipitation is facilitated by scratching the sides of the test tube with a glass rod.

3. The precipitate of magnesium ammonium phosphate on ignition gives magnesium pyrophosphate :

$$2Mg(NH_4)PO_4=Mg_2P_2O_7+2NH_3+H_2O.$$

The reaction is utilised in the gravimetric estimation of magnesium.

4. *p-Nitrobenzene-azo-resorcinol test*—The reagent is a dye, also known as of p-dihydroxybenzene-azo-p′-nitrobenzene. To a drop of magnesium test solution on a spot plate or in a test tube, add two drops of the alkaline solution of the reagent. The colour changes from violet to distinct blue, owing to the absorption of the dye on the surface of the precipitated $Mg(OH)_2$. Cobalt and nickel also respond to this test. The sensitivity of the test decreases in presence of ammonium salts and acetates.

5. *8-Hydroxyquinoline or "oxine" test.*

Place a drop of magnesium test solution on a spot plate, saturate with solid ammonium chloride and add a drop of an alkaline solution of the reagent. A greenish yellow precipitate indicates magnesium.

SODIUM AND POTASSIUM

The usual salts given are too numerous to mention. These metals are best identified by their flame tests, using a cobalt glass. A yellow flame, cut off by a cobalt glass, indicates the presence of sodium, and a flame appearing violet-red through the cobalt glass indicates the presence of potassium.

1. Potassium salts give a golden yellow crystalline precipitate with *chloroplatinic acid* in neutral or acid solutions:

$$2KCl+H_2PtCl_6=K_2PtCl_6\downarrow+2HCl,$$

or

$$2K^+ + PtCl_6^{=}=K_2PtCl_6\downarrow.$$

2. From strong solutions, *sodium hydrogen tartrate* in presence of alcohol, gives a white crystalline precipitate on scratching the sides with a glass rod.

$$KCl+\begin{array}{l}CH(OH)COONa\\ |\\ CH(OH)COOH\end{array}=\begin{array}{l}CH(OH)COOK\\ |\\ CH(OH)COOH\end{array}\downarrow+NaCl.$$

3. A potassium salt with *sodium cobaltinitrite* in acetic acid medium, gives a brilliant yellow precipitate of potassium cobaltinitrite.

$$3KNO_3+Na_3Co(NO_2)_6=K_3Co(NO_2)_6\downarrow+3NaNO_3.$$

4. *Potassium pyroantimonate* gives from neutral solutions a white crystalline precipitate of sodium pyroantimonate with a sodium salt :

$$2NaCl+K_2H_2Sb_2O_7=Na_2H_2Sb_2O_7\downarrow+2KCl$$

AMMONIUM

Ammonium salts usually given are too numerous to mention.

(1) All ammonium salts when heated with *caustic* soda, give smell of ammonia.

$$NH_4Cl+NaOH=NH_3+H_2O+NaCl,$$

or,

$$NH_4^+ + OH^- = NH_3\uparrow+H_2O.$$

(2) Ammonium salts with *chloroplatinic* acid give a golden precipitate of ammonium chloroplatinate :

$$2NH_4Cl+H_2PtCl_6=(NH_4)_2PtCl_6\downarrow+2HCl.$$

(3) With *Nessler's reagent* (formed by reacting potassium iodide, mercuric chloride and caustic potash), ammonium salts give a brown precipitate :

$$NH_4Cl+2K_2HgI_4+4KOH=IHg-OHg-NH_2 \\ +7KI+3H_2O+KCl.$$

PART II

Reactions involved in Inorganic Analysis of Acid Radicals

CHLORIDES

1. The chlorides of heavy metals, when boiled with sodium carbonate, undergo double decomposition forming sodium chloride, which comes down into the filtrate :

$$BaCl_2 + Na_2CO_3 = BaCO_3 \downarrow + 2NaCl.$$

2. All chloride solutions give a precipitate of AgCl with silver nitrate which is insoluble in nitric acid but soluble in ammonia :

$$NaCl + AgNO_3 = AgCl \downarrow + NaNO_3,$$

or,

$$Cl^- + Ag^+ = AgCl.$$

$$AgCl + 2NH_4OH = Ag(NH_3)_2Cl + 2H_2O.$$

For testing of chloride in sodium carbonate filtrate, the filtrate must be *acidified* with an excess of nitric acid, before adding silver nitrate; otherwise the white precipitate of silver carbonate will be obtained which is, however, soluble in nitric acid.

3. With manganese dioxide and concentrated sulphuric acid, the chlorides give chlorine when heated :

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2,$$

or,

$$2Cl^- + MnO_2 + 4H^+ = Mn^{++} + 2H_2O + Cl_2.$$

4. A solid chloride, mixed with potassium dichromate, and concentrated sulphuric acid, yields brownish vapours of chromyl chloride, CrO_2Cl_2, on heating :

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4$$
$$= 2CrO_2Cl_2 + 4NaHSO_4 + 2KHSO_4 + 3H_2O.$$

The vapours dissolve in water, yielding chromic acid, which gives yellow precipitate with lead acetate :

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

BROMIDES

They ought to be tested in the sodium carbonate filtrate :

$$MgBr_2 + Na_2CO_3 = MgCO_3 \downarrow + 2NaBr.$$

1. The excess sodium carbonate in the filtrate is decomposed with an excess of nitric acid, and then silver nitrate solution added, a yellow precipitate slightly soluble in ammonium hydroxide is obtained :

$$NaBr + AgNO_3 = AgBr \downarrow + NaNO_3$$
$$Br^- + Ag^+ = AgBr \downarrow .$$

2. A concentrated solution of sodium bromide when treated with concentrated nitric acid, evolves brown fumes of bromide, *colouring* the solution *yellow* (nitrous fumes, though brown, do not colour the solution yellow).

$$NaBr + HNO_3 = NaNO_3 + HBr.$$
$$8HBr + 2HNO_3 = 4Br_2 \uparrow + N_2O + 5H_2O.$$

3. Bromides when heated with manganese dioxide and concentrated sulphuric acid, give brown fumes of bromine :

$$2KBr + MnO_2 + 2H_2SO_4 = Br_2 \uparrow + K_2SO_4 + MnSO_4 + 2H_2O,$$
or $$2Br^- + MnO_2 + 4H^+ = Br_2 \uparrow + Mn^{++} + 2H_2O.$$

The fumes, being heavy, can be poured down to another test tube containing water; the solution will be coloured yellow and may be tested for bromide with silver nitrate.

4. Chlorine water, when added drop by drop, to a solution of bromide, liberates bromine. The brown solution is then shaken with chloroform or carbon disulphide; bromine dissolves in the nonaqueous layer colouring the solution brown.

$$2NaBr + Cl_2 = 2NaCl + Br_2.$$
$$2Br^+ + Cl_2 = 2Cl^- + Br_2.$$

The brown solution is changed by an excess of chlorine water, into yellowish chloride of bromine (BrCl) (difference from iodine).

IODIDES

They are also tested in the sodium carbonate filtrate: the filtrate is acidified with an *excess* of dilute sulphuric acid and sodium nitrite added, which liberates iodine; this after dilution can be tested with a fresh starch solution.

$$2NaI + 2NaNO_2 + 2H_2SO_4 = 2Na_2SO_4 + 2HI + 2HNO_2.$$
$$2HI + 2OH \cdot NO = 2H_2O + 2NO + I_2.$$
$$2I^- + 2NO_2^- + 4H^+ = 2H_2O + 2NO + I_2$$

Iodide may be completely decomposed by this reaction.

Free iodine gives blue colour with starch solution. This is due to the formation of either a blue "iodide of starch" $[C_{24}H_{40}O_{20}I]_4$ HI, or a solid solution, or iodine adsorbed by colloidal starch. It is said that the presence of hydriodic acid or a soluble iodide is necessary, before free iodine gives blue colour with starch.

2. Iodides with silver nitrate give a yellow precipitate of silver iodide, insoluble in nitric acid and ammonium hydroxide.

$$AgNO_3 + NaI = AgI \downarrow + NaNO_3,$$

or

$$Ag^+ + I^- = AgI.$$

3. Mercuric chloride with sodium iodide forms a yellow precipitate, changing to deep red. The precipitate is soluble in an excess of sodium iodide.

$$2NaI + HgCl_2 = HgI_2 \downarrow + 2NaCl,$$

$$2I^- + Hg^{++} = HgI_2 \downarrow .$$

4. Iodides, when heated with manganese dioxide and concentrated sulphuric acid, liberate iodine :

$$2KI + MnO_2 + 2H_2SO_4 = MnSO_4 + I_2 + K_2SO_4 + 2H_2O,$$

or

$$2I^- + MnO_2 + 4H^+ = Mn^{++} + I_2 + 2H_2O.$$

5. Chlorine water added, drop by drop, to an iodide solution liberates iodine :

$$2KI + Cl_2 = I_2 + 2KCl,$$

or

$$2I^- + Cl_2 = I_2 + 2Cl^-.$$

Iodine is more soluble in chloroform or carbon disulphide, than in water, and therefore, when the mixture is shaken with this solvent, iodine passes to the non-aqueous bottom layer colouring violet. The colour disappears on adding a further quantity of chlorine water as iodine is oxidised to colourless iodic acid :

$$I_2 + 6H_2O + 5Cl_2 = 2HIO_3 + 10HCl.$$

Test of bromide and iodide in presence of each other—

To the mixed solution, add a few drops of chloroform and then chlorine water, drop by drop, and shake.

(*i*) If chloroform is not coloured—bromide and iodide both absent. Test for chloride with $AgNO_3$.

(*ii*) If the chloroform layer is brown—iodide is absent and bromide present.

(*iii*) If the chloroform layer is violet—iodide present. Add more chlorine water, the violet layer would disappear; and now if brown layer appears, bromide is also present.

Testing of chloride in presence of bromide and iodide.

In the sodium carbonate filtrate, the iodide is decomposed adding excess of dilute sulphuric acid and sodium nitrite; $2HI + 2HNO_2 = 2H_2O + 2NO + I_2$. When free from iodide, concentrate the solution, and decompose the bromide by concentrated nitric acid :

$$8NaBr + 10HNO_3 = 4Br_2 \uparrow + N_2O \uparrow + 8NaNO_3 + 5H_2O.$$

After decomposing the bromide, one can test for chloride by adding silver nitrate :

$$NaCl + AgNO_3 = AgCl \downarrow + NaNO_3.$$

FLUORIDES

1. All fluorides when heated with concentrated sulphuric acid and sand, evolve silicon tetrafluoride gas. On holding a moistened glass rod in the vapours, water reacts with the gas to give a white deposit of silicic acid :

$$H_2SO_4 + CaF_2 = H_2F_2 \uparrow + CaSO_4,$$
$$2H_2F_2 + SiO_2 = SiF_4 \uparrow + 2H_2O.$$
$$3SiF_4 + 3H_2O = \underset{\text{Silicic acid}}{H_2SiO_3} \downarrow + \underset{\text{Hydrcfluosilicic acid}}{2H_2SiF_6}.$$

2. Calcium chloride gives a precipitate of calcium fluoride with a soluble fluoride (to be tested in the sodium carbonate filtrate) :

$$2NaF + CaCl_2 = CaF_2 \downarrow + 2NaCl.$$
$$2F^- + Ca^{++} = CaF_2 \downarrow .$$

The precipitate is insoluble in acetic acid, but dissolves in mineral acids.

3. *Zirconium-Alizarin lake test.*—(*a*) Immerse filter paper in a 5% solution of zirconium nitrate in 5% HCl; drain and place in 2% aqueous solution of alizarin-S. Wash the paper till the washings are colourless. The paper is coloured red-violet. Moisten the paper with 50% acetic acid, and place a drop of the neutral test solution on moist red spot. The spot will turn yellow if fluoride is present.

(*b*) The test may be done in semimicro test-tubes also. Take 2 drops of 0.1% aqueous solution of alizarin-S (sodium alizarin sulphonate), and zirconyl nitrate (10·1 g. solid dissolved in 20 ml. conc. HCl and diluted to 100 ml. with water) : add 2 drops of the fluoride solution. The zirconium lake is decolourized to a clear yellow solution.

CHLORATES

1. Chlorates do not give a precipitate with silver nitrate, because silver chlorate is soluble.

2. Chlorates, when treated with dilute sulphuric acid and zinc, are reduced to chlorides, which then give a precipitate with silver nitrate :

$$KClO_3+6H=KCl+3H_2O.$$
$$KCl+AgNO_3=AgCl\downarrow+KNO_3.$$

Reduction may be accomplished with sulphurous acid or with sodium nitrite in the presence of dil. H_2SO_4. The nitrite should be free from chloride.

$$KClO_3+3NaNO_2=KCl+3NaNO_3.$$

3. When concentrated sulphuric acid is added to a solid chlorate, the mass is coloured yellow on account of the liberation of ClO_2; on warming the mixture, the cracking noise ensues (may give rise to explosion, if the quantity taken is not small).

$$3KClO_3+2H_2SO_4=2ClO_2+2KHSO_4+KClO_4+H_2O.$$

or

$$3ClO_3^-+2H^+=2ClO_2+H_2O+ClO_4.$$

4. *Indigo test.* To the chlorate solution, add a sufficient quantity of indigo, dissolved in concentrated sulphuric acid, to give a light blue colour. Add a little dilute sulphuric acid and introduce drop by drop a little sodium sulphite solution. The blue colour will disappear quickly.

$$2H_2SO_3+HClO_3=2H_2SO_4+HClO.$$

The hypochlorous acid bleaches indigo.

CYANIDES [Danger]

1. Dilute sulphuric acid decomposes all the cyanide solutions (mercuric is an exception), setting HCN free in the cold. It is dangerous to recognize it by smell, as it is highly poisonous.

The insoluble cyanides are decomposed by dilute sulphuric acid in hot.

2. If silver nitrate is added to a solution of a cyanide drop by drop, a precipitate is formed on the addition of each drop, but is soluble on shaking, *i.e.*, in excess of the cyanide solution :

$$CN^-+Ag^+=AgCN\downarrow$$
$$AgCN+CN^-=[Ag(CN)_2]^-$$

3. Ferrous sulphate solution gives with a soluble cyanide, a precipitate of ferrous cyanide, which again reacts with the excess of cyanide solution, giving a ferrocyanide :

$$Fe^{++}+2CN^{-}=Fe(CN)_2$$
$$Fe(CN)_2+4CN^{-}=Fe(CN)_6^{----}$$

The ferrocyanide, on addition of ferric chloride, yields Prussian blue colour or precipitate.

4. Cyanides, when fused with sulphur, or their solution evaporated with a little yellow ammonium sulphide on a porcelain dish, yield *thiocyanate*.

$$KCN+(NH_4)_2S_2=(NH_4)_2S+KCNS$$

Boil the solution now with hydrochloric acid and add a few drops ferric chloride solution. A red coloration would indicate the formation of thiocyanate.

FERROCYANIDES

1. Ferrocyanides, when heated with concentrated sulphuric acid, evolve carbon monoxide which burns with a blue flame :

$$K_4Fe(CN)_6+11H_2SO_4+6H_2O$$
$$=FeSO_4+4KHSO_4+6NH_4HSO_4+6CO\uparrow.$$

2. With silver nitrate solution, ferrocyanides give a white precipitate of $Ag_4Fe(CN)_6$, which is insoluble in dilute nitric acid and in ammonia (but is soluble in potassium cyanide solution).

$$Fe(CN)_6^{----}+4Ag^{+}=Ag_4Fe(CN)_6\downarrow.$$

3. Cupric sulphate, $CuSO_4$, gives a brown precipitate of $Cu_2Fe(CN)_6$ with ferrocyanides in presence of acetic acid.

4. Zinc sulphate gives a white precipitate of $[K_2Zn_3(FeCN)_6]_2$ with ferrocyanides. The precipitate is insoluble in dilute acids, but soluble in caustic alkali solutions.

$$K_2Zn_3[Fe(CN)_6]_2+12OH^{-}$$
$$=2[Fe(CN)_6]^{----}+3ZnO_2^{--}+2K^{+}+6H_2O.$$

5. Ferric chloride solution gives deep Prussian blue colour or precipitate with soluble ferrocyanides. (Ferrous salts give only a light blue colour, which intensifies on exposure to air).

6. If the given ferrocyanide is an insoluble substance, boil it with caustic soda; the insoluble metallic hydroxide and sodium ferrocyanide will be formed. Filter off the insoluble portion and

add dilute HCl to the filtrate and a few drops of ferric chloride solution. Prussian blue colour will appear if a ferrocyanide is present.

FERRICYANIDES

1. Ferricyanides, when heated with concentrated sulphuric acid, evolve carbon monoxide (cf. ferrocyanides) :

$$K_3Fe(CN)_6+11H_2SO_4+6H_2O$$
$$=FeH(SO_4)_2+3KHSO_4+6NH_4H.\ SO_4+6CO\uparrow.$$

2. With silver nitrate solution, ferricyanides give orange coloured silver ferricyanide :

$$Fe(CN)_6^{---}+3Ag^+=Ag_3Fe(CN)_6\downarrow.$$

The precipitate is insoluble in nitric acid, but soluble in ammonia.

3. Ferrous sulphate solution gives a deep Turnbull's blue precipitate with ferricyanides, in neutral and acid solutions.

4. Cupric sulphate gives a green precipitate of cupric ferricyanide :

$$2Fe(CN)_6^{---}+3Cu^{++}=Cu_3[Fe(CN)_6]_2.$$

5. Ferricyanides, in alkaline solutions, are reduced to ferrocyanides by sulphides, iodides, sulphites, ferrous and manganous salts, H_2O_2 and starch.

$$2Fe(CN)_6^{---}+S^{=}=2Fe(CN)_6^{==}+S\downarrow.$$
$$2Fe(CN)_6^{---}+2I^-=2Fe(CN)_6^{==}+I_2.$$
$$2Fe(CN)_6^{---}+H_2O_2+2OH^-=2Fe(CN)_6^{==}+2H_2O+O_2\uparrow.$$

CARBONATES

Carbonates, when treated with dilute acids, effervesce, and carbon dioxide evolves :

$$BaCO_3+2HCl=BaCl_2+H_2O+CO_2\uparrow,$$

or, $$CO_3^{=}+2H^+=H_2O+CO_2\uparrow.$$

The gas turns lime water milky :

$$Ca(OH)_2+CO_2=CaCO_3\downarrow+H_2O.$$

On passing excess of CO_2, the milky precipitate dissolves forming a bicarbonate.

$$CaCO_3+CO_2+H_2O\rightarrow Ca(HCO_3)_2$$

BICARBONATES

Test with sodium or potassim bicarbonate sample.

1. To the cold solution of a bicarbonate, say $NaHCO_3$, add a solution of magnesium sulphate. No precipitate apears in cold. Now boil the solution. A white precipitate of $MgCO_3$ is obtained:

$$2NaHCO_3+MgSO_4=Mg(HCO_3)_2+Na_2SO_4,$$
$$Mg(HCO_3)_2 \rightleftharpoons MgCO_3\downarrow+H_2O+CO_2.$$

2. The solutions of bicarbonates on boiling evolve CO_2 gas (test with lime water).

3. Add mercuric chloride solution to a solution of bicarbonate. No precipitate is furnished, (Normal carbonates give a reddish-brown precipitate of basic carbonate, $Hg_4O_3 \cdot CO_3$ in the cold):

$$4Na_2CO_3+4HgCl_2=Hg_4O_3CO_3+8NaCl+3CO_2.$$

Test for bicarbonate in presence of a carbonate—To the mixed solution of the two, add excess of calcium chloride solution. All carbonate will be precipitated (a part of the bicarbonate is also precipitated as $CaCO_3$). Filter rapidly and to the clear filtrate, add a little ammonia solution. A white precipitate or turbidity indicates the presence of a bicarbonate.

OXALATES

1. Solid oxalates on ignition change to carbonates and oxides :

$$CaC_2O_4=CaCO_3+CO\uparrow.$$
$$CaCO_3=CaO+CO_2\uparrow.$$

2. Oxalates when heated with concentrated sulphuric acid, evolve carbon monoxide (which burns with a pale blue flame) and carbon dioxide :

$$BaC_2O_4+H_2SO_4=BaSO_4+H_2O+CO\uparrow+CO_2\uparrow.$$

3. Acidify the sodium carbonate filtrate with an *excess* of acetic acid, and add calcium chloride. Calcium oxalate is precipitated :

$$CaCl_2+Na_2C_2O_4=CaC_2O_4\downarrow+2NaCl.$$

Filter out this precipitate and treat it with an excess of dilute sulphuric acid and potassium permanganate and warm. If the colour disappears, oxalic acid is confirmed :

$$CaC_2O_4+H_2SO_4+O=CaSO_4+H_2O+2CO_2\uparrow.$$

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$$2NaHCO_3+MgSO_4=Mg(HCO_3)_2+Na_2SO_4,$$
$$Mg(HCO_3)_2\rightleftharpoons MgCO_3\downarrow+H_2O+CO_2.$$

2. The solutions of bicarbonates on boiling evolve CO_2 gas (test with lime water).

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Filter out this precipitate and treat it with an excess of dilute sulphuric acid and potassium permanganate and warm. If the colour disappears, oxalic acid is confirmed :

$$CaC_2O_4+H_2SO_4+O=CaSO_4+H_2O+2CO_2\uparrow.$$

4. To the oxalate (solution or powder), add dilute sulphuric acid (if a carbonate is also present, add an excess of the acid till all effervescence ceases). Now warm and add a pinch of manganese dioxide. If a fresh effervescence ensues, the oxalate is confirmed. Manganese dioxide liberates carbon dioxide from oxalates :

$$CaC_2O_4+MnO_2+2H_2SO_4=CaSO_4+MnSO_4+2CO_2\uparrow+2H_2O,$$

or $$C_2O_4^{=}+MnO_2+4H^+=2CO_2\uparrow+Mn^{++}+2H_2O.$$

SULPHIDES

1. All sulphides, with the exception of a few (as of Hg, Ag and As), when treated with dilute sulphuric acid, evolve hydrogen sulphide gas, which gives black stain on lead acetate paper.

$$FeS+H_2SO_4=FeSO_4+H_2S\uparrow.$$
$$(CH_3COO)_2Pb+H_2S=2CH_3COOH+PbS\downarrow.$$

2. Some of the insoluble sulphides, like mercuric, liberate hydrogen sulphide when treated with nascent hydrogen (zinc and dilute sulphuric acid).

$$Zn+H_2SO_4\rightarrow ZnSO_4+2H.$$
$$HgS+2H\rightarrow H_2S\uparrow+Hg.$$

3. When sulphides are shaken with lead carbonate in presence of water, they produce black lead sulphide. The reaction is used in identifying a sulphide in presence of sulphite and sulphate :

$$PbCO_3+Na_2S\rightleftharpoons Na_2CO_3+PbS.$$

4. Sulphides, in presence of *alkali*, produce a violet or purple coloration with a fresh solution of sodium nitroprusside, $Na_2Fe(NO)(CN)_5$:—take a drop of each of the reactants, and perform the test on a watch glass.

$$Na_2S+Na_2[Fe(CN)_5NO]=Na_4[Fe(CN)_5NOS].$$

5. *Methylene blue test*—To the sulphide, add one-fourth of its volume of concentrated hydrochloric acid, and a trace of dimethyl-para phenylenediamine sulphate, $NH_2.C_6H_4.N(CH_3)_2.H_2SO_4$; shake and add one or two drops of a dilute solution of ferric chloride. A blue colour will appear, due to formation of methylene blue. (If too little HCl is present, a red coloration is obtained).

1. Sulphites, when heated with dilute sulphuric acid, give off sulphur dioxide, which produces a green coloration on a filter paper moistened with potassium dichromate solution.

$$Na_2SO_3+H_2SO_4=H_2O+SO_2\uparrow+Na_2SO_4,$$

$$3SO_2+K_2Cr_2O_7+H_2SO_4=Cr_2(SO_4)_3+K_2SO_4+H_2O,$$

or $$3SO_3^{=}+8H^++Cr_2O_7^{=}=3SO_4^{=}+4H_2O+2Cr^{+++}.$$

The green colour is due to the formation of chromic salts, obtained by the reduction of $Cr_2O_7^{=}$ with SO_2 gas.

2. Sulphites decolourise a solution of potassium permanganate, in presence of dilute H_2SO_4.

$$5SO_2+2KMnO_4+2H_2O=K_2SO_4+2MnSO_4+2H_2SO_4,$$

or $$5SO_2+2MnO_4^-+2H_2O=5SO_4^{=}+2Mn^{++}+4H^+.$$

3. *Sodium nitroprusside and zinc sulphate test*—A neutral sulphite solution is treated with a dilute solution of sodium nitroprusside, a faint pink colour is produced. The colour becomes distinct red on adding a considerable quantity of zinc sulphate.

4. Sulphites are converted to sulphates by bromine water.

$$Na_2SO_3+Br_2+H_2O=Na_2SO_4+2HBr,$$

or $$SO_3^{=}+Br_2+H_2O=SO_4^{=}+2Br^-.$$

This reaction is used in identifying a sulphite in presence of a sulphate. The mixture is acidified with hydrochloric acid and barium chloride added. Barium sulphate is precipitated, whereas, barium sulphite, which is soluble, is retained in the solution. The filtrate, containing the sulphite, is then treated with bromine water; it is thus oxidised to sulphate and gives a precipitate of barium sulphate.

SULPHATES

1. The test is made in sodium carbonate filtrate :

$$PbSO_4+Na_2CO_3\rightleftharpoons PbCO_3+Na_2SO_4.$$

The filtrate is acidified with an excess of dilute hydrochloric acid, and treated with a solution of barium chloride. A white precipitate is obtained which is insoluble in concentrated acids.

$$Na_2SO_4+BaCl_2=2NaCl+BaSO_4\downarrow.$$

2. All the sulphates, when heated with charcoal and fusion mixture, are converted to sodium sulphide :

$$SrSO_4+2C+Na_2SO_3=Na_2S+SrCO_3+2CO_2.$$

The sulphide may be tested with sodium nitroprusside.

THIOSULPHATES

1. All the thiosulphates, when treated with dilute hydrochloric acid, give a yellowish precipitate of sulphur and liberate sulphur dioxide :

$$Na_2S_2O_3+2HCl=2NaCl+SO_2+S+H_2O.$$

2. Ferric chloride gives a reddish violet colour with alkali thiosulphates.

$$3Na_2S_2O_3+2FeCl_3=Fe_2(S_2O_3)_3+6NaCl.$$

The colour disappears on warming.

3. Thiosulphates decolourise a solution of iodine, forming sodium tetrathionate :

$$2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI.$$

or $$2S_2O_3^{=}+I_2=S_4O_6^{=}+2I^{-}.$$

4. Silver nitrate, with a thiosulphate, gives a white precipitate of silver thiosulphate. The precipitate is soluble in an excess of sodium thiosulphate.

$$2AgNO_3+Na_2S_2O_3=2NaNO_3+Ag_2S_2O_3,$$
$$Ag_2S_2O_3+2Na_2S_2O_3=Na_4[Ag_2(S_2O_3)_3].$$

Silver thiosulphate, on warming or on the addition of dilute acids, first turns yellow, then brown and finally black, due to the formation of Ag_2S.

$$Ag_2S_2O_3+H_2O=Ag_2S+H_2SO_4.$$

Detection of sulphide, sulphite, sulphate and thiosulphate in a mixture:

The solution must not be *acidified*, otherwise sulphites and thiosulphates will be decomposed.

(*i*) Shake up the sodium carbonate filtrate with lead carbonate. Sulphide is thus removed. Filter off the lead sulphide and carbonate :

$$PbCO_3+Na_2S\rightarrow PbS\downarrow+Na_2CO_3.$$

To the filtrate, add excess of barium chloride, and filter. The precipitate consists of barium sulphite and barium sulphate. The thiosulphate remains in the filtrate.

Treat the mixed precipitates of sulphate and sulphite with hydrochloric acid. Barium sulphite goes into the solution, leaving barium sulphate on the filter paper. Treat the solution with bromine water; sulphite is converted to sulphate and barium sulphate precipitated.

The thiosulphate filtrate is treated with dilute hydrochloric acid and warmed. Sulphur is precipitated, and sulphur dioxide is evolved.

Na_2S, Na_2SO_3, Na_2SO_4, $Na_2S_2O_3$
| $PbCO_3$ and filter

- Black residue
  PbS
  SULPHIDE
- Filtrate
  | $BaCl_2$ and filter
  - Residue
    $BaSO_3$, $BaSO_4$
    | HCl
    - Residue
      SULPHATE
    - Filtrate
      | Br_2 water
      Precipitate
      SULPHATE
  - Filtrate
    $Na_2S_2O_3$
    | add HCl
    $S+SO_2$
    THIOSULPHATE

NITRITES

1. All the mineral acids, and even the acetic acid, decompose nitrites to nitric oxide, nitrogen peroxide (with air), and nitric acid :

$$2NaNO_2+H_2SO_4=Na_2SO_4+2HNO_2,$$
$$3HNO_2=HNO_3+2NO+H_2O,$$
$$2NO+O_2=2NO_2.$$

2. Ferrous sulphate solution and sulphuric acid, with a solution of nitrite, react to give a brown coloration. Nitric oxide generated in the reaction (1) is absorbed by ferrous sulphate, forming $2FeSO_4.NO$(cf. ring test for nitrates).

3. All nitrites evolve iodine from potassium iodide in presence of dilute mineral acids. The iodide may be tested with starch solution (blue colour) :

$$KI+KNO_2+H_2SO_4=HI+HNO_2+K_2SO_4$$
$$2HI+2HNO_2=2H_2O+2NO+I_2,$$

or

$$2NO_2^-+2I^-+4H^+=2NO+2H_2O+I_2.$$

4. Nitrites, when heated with urea and dilute sulphuric acid, are decomposed to nitrogen :

$$CO(NH_2)_2+2OH.NO=2N_2+3H_2O+CO_2.$$

When the decomposition is complete, the test (3) is not answered. The method is used in the detection of nitrates in presence of nitrites.

5. A solution of nitrite, when boiled for sometime with a fair concentration of ammonium chloride, is decomposed to nitrogen :

$$NaNO_2 + NH_4Cl = NaCl + 2H_2O + N_2.$$
$$NO_2^- + NH_4^+ = N_2 + 2H_2O.$$

This reaction is also utilised in decomposing nitrites completely, before a test for nitrates could be made. For a complete decomposition, the process has to be repeated a number of times, until the test (3) is no longer given.

NITRATES

All the tests for nitrates are essentially the tests for nitrites. The nitrates are first reduced to nitrites, and then they are tested as given above. It is, therefore, essential to see that the solution does not contain a nitrite before the test of nitrates is undertaken. In case a nitrite is originally present, it has to be completely decomposed by heating with an excess of ammonium chloride, or with urea and dilute sulphuric acid.

1. All nitrates when heated with copper turnings and concentrated sulphuric acid give nitric oxide, which changes to brown peroxide fumes in contact with air.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O,$$
$$2NO + O_2 = 2NO_2.$$

2. To a mixture of ferrous sulphate and nitrate solutions, if concentrated sulphuric acid is carefully poured down the side of a test tube, and the mixture cooled, a brown ring is formed at the junction.

Ferrous sulphate, at first, reduces the nitrate to nitrite and then to nitric oxide. This oxide is absorbed by the unoxidised portion of ferrous sulphate :

$$2NaNO_3 + 4H_2SO_4 + 6FeSO_4 = Na_2SO_4 + 2NO + 3Fe_2(SO_4)_3 + 4H_2O.$$
$$\underset{\text{(brown)}}{2FeSO_4 + NO = 2FeSO_4.NO.}$$

3. Nitrates may be reduced to nitrites by the action of zinc and dilute sulphuric acid :

$$KNO_3 + Zn + H_2SO_4 = KNO_2 + ZnSO_4 + H_2O.$$

The mixture is added to a solution of potassium iodide and starch. The iodine evolved gives the blue colour :

$$2HNO_2 + 2HI = I_2 + 2NO + 2H_2O.$$

ACETATES

1. As almost all the acetates are fairly soluble in water, the aqueous extract of the given mixture is taken. It is cooled and to the neutral solution is added a neutral solution of ferric chloride. A deep red coloration in cold indicates the presence of an acetate.

$$FeCl_3 + 3CH_3COONa = Fe(CH_3COO)_3 + 3NaCl.$$

2. All the acetates, when boiled with concentrated or dilute sulphuric acid, give the characteristic vinegar smell of acetic acid:

$$2CH_3COONH_4 + H_2SO_4 = 2CH_3COOH + (NH_4)_2SO_4.$$

PHOSPHATES

The only reliable test for phosphates is the one with ammonium molybdate and nitric acid. The mixture of the three on warming gives a canary yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$.

This test is also answered by arsenates which under the very conditions, give the similar yellow precipitate of ammonium arseno-molybdate, $(NH_4)_3AsO_4.12MoO_3$. Therefore, in presence of arsenic the test of phosphates is unreliable. When arsenic is present, it is at first removed in the Second Group analysis, and the the filtrate of the Second Group is tested for phosphates.

BORATES

A borate mixture is stirred in a porcelain dish with a small amount of concentrated sulphuric acid, and a little ethyl alcohol added. When a flame is applied to the mixture, alcohol burns with a green-edged flame. A volatile compound, ethyl borate, is formed which burns with the green flame. Presence of copper salts interferes with the test , because they also produce green-edged flame.

$$Na_2B_4O_7 + H_2SO_4 = H_2B_4O_7 + Na_2SO_4,$$
$$H_2B_4O_7 + 5H_2O = 4H_3BO_3.$$
$$H_3BO_3 + 3C_2H_5OH \rightleftharpoons B(OC_2H_5)_3 + 3H_2O.$$

CaF_2 test for borates:—

Make a paste of the borate with some calcium fluoride and a little concentrated sulphuric acid. Hold a part of this paste with the help of a platinum wire or with a glass rod near the edge of a Bunsen burner. Volatile BF_3 is formed and colours the flame green. Copper salts do not interfere with this test.

$$CaF_2+H_2SO_4 \rightleftharpoons CaSO_4+2HF,$$
$$Na_2B_4O_7+H_2SO_4 \rightleftharpoons 2B_2O_3+Na_2SO_4+H_2O,$$
$$B_2O_3+6HF \rightleftharpoons 2BF_3\uparrow+3H_2O.$$

SILICATES

1. Silicates and silica, when heated on *charcoal* and moistened with cobalt nitrate, and again heated give a blue mass on *fusion*. The test is given by alumina, borates and phosphates also.

2. Mix the substance to be tested for silicate with *calcium or potassium fluoride* in a lead crucible. Silicon tetrafluoride is produced on heating the mixture with concentrated sulphuric acid:

$$CaF_2+2H_2SO_4+SiO_2=2CaSO_4+SiF_4\uparrow+2H_2O.$$

On holding a moist glass rod in the fumes of the tetrafluoride, a white deposit of silicic acid is formed on the rod.

$$3SiF_4+4H_2O=H_4SiO_4\downarrow+2H_2SiF_6$$

3. Silica and silicates do not dissolve when heated in a *microcosmic bead.* Silica particles are seen floating in the transparent bead.

4. Silicates and silica form soluble silicates when fused with *sodium carbonate.*

5. A soluble silicate with *hydrochloric acid,* liberates colloidal silicic acid; this on evaporation leaves insoluble silica gel.

6. A soluble silicate gives with *silver nitrate* solution an orange-red precipitate of silver silicate.

$$SiO_3^{=}+2Ag^{+}=Ag_2SiO_3\downarrow.$$

Examination Questions

1. (*a*) Explain the use of potassium cyanide solution in qualitative analysis.

(*b*) Give a scheme for detecting elements of Group 3 and 4 in the presence of phosphate with a short explanatory note.

(*c*) How will you detect an arsenate and chromate when present together, and a carbonate and oxalate when present together?
(*Alld. Univ., B Sc.*, 1935)

[On passing sulphur dioxide through the solution, arsenate is reduced to arsenite and chromate to a chromium salt. Arsenite gives a precipitate of arsenious sulphide in the Second Group, and chromium is tested in the Third Group as usual.]

2. Explain the following with equations:—

(*i*) Why phosphate and organic matter are removed before proceeding to the Third Group.

(*ii*) Why yellow ammonium sulphide is used instead of ordinary ammonium sulphide in the separation of Cu-As Groups ?
(*Alld. Univ., B.Sc.*, 1936)

3. Write a note on solubility product and its applications in analytical chemistry. (*Alld. Univ., B.Sc.*, 1936)

4. Describe with full details the various reactions involved in the separation of the Second Group B metals in the qualitative analysis. (*Alld. Univ., B.Sc.*, 1940)

5. Discuss the various reactions involved in the separation of phosphoric acid before proceeding to the separation of the metals after the Second Group in the qualitative analysis.
(*Alld. Univ., B.Sc.*, 1940)

6. What are the interfering acids in the qualitative analysis of the basic radicals? How do they interfere? Give the methods of removing them in the group analysis for metals. Give all relevant equations. (*Alld. Univ., B.Sc.*, 1939)

7. Explain the term "available oxygen" as applied to potassium permanganate and manganese dioxide. How is it estimated?

(*b*) How would you identify the following salts: silver chloride, stannic oxide and barium sulphate ? Give necessary equations.
(*Alld. Univ., B.Sc.*, 1938)

8. Explain the principles involved in the use of the following in qualitative analysis:—

(*a*) Addition of ammonium chloride and ammonium hydroxide before the precipitation of the Third Group.

(*b*) Addition of sodium acetate and acetic acid in presence phosphate.

(*c*) Addition of sodium bicarbonate and bromine water in the detection of cobalt and nickel.

(*d*) The reason why dilution is advised in precipitating metals of the Second Group. (*Alld. Univ., B.Sc.* 1937)

9. Give the chemistry of the following processes in analytical chemistry:—(*a*) Removal of phosphoric acid from a mixture of inorganic salts. (*b*) Identification of cobalt and nickel ions in presence of each other.
(*Alld. Univ., B.Sc.*, 1942)

10. (*a*) What is ammonium polysulphide? Why is it necessary to use it in order to separate Copper from Arsenic Groups? Give necessary equations.

(*b*) How do you test for cadmium in presence of copper? Give equations for reactions. (*Alld. Univ., B.Sc.*, 1944)

11. Discuss fully the chemistry of the identification and separation in qualitative analysis of (*a*) copper and cadmium, (*b*) aluminium and chromium, (*c*) chloride and bromide, and (*d*) nitrate and nitrite. Give equations. (*Agra Univ., B.Sc.* 1942)

12. (*a*) Explain clearly the use of ammonium chloride in qualitative analysis. (*b*) How do you prepare sodium thiosulphate? Explain its various uses.

(*Agra Univ., B.Sc.*, 1942)

13. Draw up a scheme for the qualitative analysis of a mixture containing the following radicals: nickel, cobalt, phosphate and fluoride. Explain the steps and give equations of the reactions involved. (*Agra Univ., B.Sc.*, 1943)

14. (*a*) Complete the following equations:—

(*i*) $As_2S_3+(NH_4)_2CO_3=$

(*ii*) $FeSO_4+H_2SO_4+HNO_3=$

(*iii*) $KMnO_4+H_2SO_4+(COOH)_2=$

(*iv*) $Na_2S_2O_3+I_2=$

(*b*) How do you explain the following observations in qualitative analysis?

(*i*) Formation of a white precipitate in the Second Group in the absence of any of the members of the group.

(*Ans.*—Hydrogen sulphide has been oxidised to sulphur by some oxidising substance.)

(*ii*) Formation of a white crystalline precipitate when concentrated hydrochloric acid is added to a concentrated solution of barium chloride. (*Ans.*—The precipitate is of crystalline $BaCl_2$. Apply the concept of solubility product, similar to the precipitation of NaCl (saturated) on the addition of HCl).

(*Agra Univ., B.Sc.*, 1943)

15. How will you identify (*a*) chloride, bromide, and iodide in presence of each other, (*b*) copper and cadmium in a mixture, and (*c*) chromium in a solution of potassium chromate?

(*Agra Univ., B.Sc.*, 1944)

16. Give a general account of some of the familiar complex salts specially those involving reactions with ammonia and potas-

sium cyanide. How do you use these reactions in analytical chemistry? (*Agra Univ.*, *B.Sc.*, 1944)

17. Discuss the use of sulphuretted hydrogen in analysis. How does the gas act on the following:—

(*a*) an acidified solution of (*i*) potassium dichromate; (*ii*) potassium permanganate;

(*b*) solution of zinc sulphate containing sodium acetate;
(*c*) milk of lime.

Discuss the reactions involved from the ionic standpoint as far as possible. (*B. H. U.*, *B.Sc*, 1929)

18. How would you detect—(*i*) a nitrite and a bromide in a mixture of the two; (*ii*) a nitrite and a sulphide in a mixture of the two; (*iii*) a chloride, a bromide and an iodide in a mixture of the three; (*iv*) a sulphide, a sulphite and a sulphate in a mixture of the three. Give very clear and definite tests.

(*U. P. C. S.* 1939)

19. How do you explain the following facts: (*i*) The addition of nitric acid to a concentrated solution of barium nitrate brings about a precipitation. (*Ans.*—Apply sloubility product).

(*ii*) Disodium hydrogen phosphate is neutral to litmus and alkaline to methyl orange. (*Ans.*—Apply theory of indicator and pH considerations).

(*iii*) Zinc sulphide is precipitated by hydrogen sulphide from a solution of zinc acetate but not from a solution of zinc chloride.

(*iv*) Sodium bicarbonate is alkaline to litmus and netural to phenolphthalein.

(*v*) Hydrogen sulphide is vey much weaker acid than sulphuric, and it will precipitate copper sulphide from a solution of copper sulphate (*Ans.*—CuS having a low solubility product is removed from the field of action). (*U. P.C. S.*, 1939)

20. How can one test for : (*a*) a nitrate in presence of a nitrite; (*b*) a sulphide in presence of a thiosulphate; (*c*) each gas in a mixture of carbon monoxide, carbon dioxide and sulphur dioxide; (*d*) a phosphate in presence of an arsenate. Give experimental instructions and explanatory equations. (*I.C.S.*, 1933)

21. Give a scheme for the identification and separation of zinc, manganese, nickel and cobalt in a mixture containing phosphates. Explain the reactions involved.

(*Agra Univ.*, *B.Sc.*, 1923, 1938, 1941)

22. Discuss the uses of the following reagents in systematic qualitative analysis—(*a*) potassium cyanide, (*b*) ammonium chloride, (*c*) ammonium sulphide.

(*Agra Univ., B.Sc.*, 1940)

23. Decribe the method you would adopt for the identification and separation of the following metals in a mixture of their chlorides:—(*a*) sodium and potassium; (*b*) nickel and cobalt. Explain the reactions. (*Agra Univ., B.Sc.*, 1939)

24. How will you explain the following observations in qualitative analysis:—(*i*) A white precipitate is obtained in the Second Group. (*ii*) A precipitate is obtained in the Iron Group by the addition of ammonium chloride and ammonium hydroxide, in the absence of iron, aluminium and chromium.

(*Agra Univ., B.Sc.*, 1938)

25. Devise a scheme for the qualitative analysis of a mixture containing the following radicals: antimony, tin, bromide, chloride and nitrate. Explain the reactions.

(*Agra Univ., B.Sc.*, 1937)

26. Explain clearly why it is necessary to remove phosphates and oxalates before proceeding to the Third Group in qualitative analysis. (*Agra Univ., B. Sc.*, 1940, 1937)

27. Devise a scheme for the qualitative analysis of a mixture containing nickel, cobalt, phosphate and fluoride radicals. Explain the reactions. (*Agra Univ., B.Sc.*, 1936)

28. (*a*) Complete the following equations:—

(*i*) $Cr(OH)_3+Na_2CO_3+KNO_3=$

(*ii*) $KMnO_4$(alkaline)$+KI+H_2O=$

(*iii*) $As_2S_3+(NH_4)_2S_2=$

(*iv*) $FeSO_4+H_2SO_4+HNO_3=$

(*b*) How do you account for the following observations:

(*i*) Formation of a yellowish precipitate in the Second Group in the absence of any of the members of the group.

(*ii*) Formation of a brownish precipitate in the Iron Group in the absence of iron, aluminium and chromium.

(*Agra Univ., B. Sc.*, 1936)

29. Explain clearly the use of (*a*) hydrogen sulphide, and (*b*) ammonium chloride, in qualitative analysis.

(*Agra Univ., B. Sc.*, 1935)

30. Explain, giving equations, the action of ammonium hydroxide on solutions of (*i*) copper sulphate, (*ii*) cadmium sulphate and (*iii*) silver nitrate.

(*b*) How would you detect the presence of a chloride, in a mixture containing chloride and a bromide, both being soluble in water. (*Agra Univ., B.Sc.*, 1935)

31. Give the principles on which the separation of elements into groups in qualitative analysis depends. Discuss in detail the separation of the radicals of the Group II-A.
(*Agra Univ., B.Sc.*, 1934)

32. State how you would proceed to analyse a mixture containing a phosphate. Explain the steps and give equations of the reactions involved.
(*Agra Univ., B.Sc.*, 1932)

33. What are the reactions involved in the qualitative separation of tin from arsenic.
(*Agra Univ., B.Sc.*, 1931)

34. Explain why the sulphides of iron, zinc or manganese are not precipitated in the Second Group. How will you identify nickel in presence of cobalt?
(*Agra Univ., B.Sc.*, 1945)

35. How will you proceed on with the qualitative analysis of a mixture which contains magnesium, phosphate, sulphide, sulphite and sulphate radicals? Give necessary equations.
(*Agra Univ., B. Sc.*, 1946)

36. Explain fully with equations the functions of ammonium chloride when added to ammonium hydroxide; sodium acetate when added to acetic acid and the addition of nitric acid before proceeding to the separation of Iron and subsequent Groups.
(*Alld. Univ., B.Sc.*, 1945)

37. Show how the following metals could be detected in a mixture of their salts. Give the chemistry of the processes involved.

(*a*) Copper and cadmium;

(*b*) Aluminium and chromium.

(*c*) Cobalt and nickel. (*Alld. Univ., B.Sc.* 1946)

PART III

Inorganic Qualitative Analysis

SECTION I

Examination of basic radicals—The basic radicals of a mixture are identified by applying dry tests to the solid material and wet tests to the substance in solution.

Dry tests—Dry tests give us only a preliminary idea of the nature of the substances present. They are more useful in case of single salts, and, therefore, in the analysis of a mixture they should be employed as confirmatory tests to the individual precipitates and not to the whole mixture. There are quite a large number of dry tests, but the most important and useful ones are given below.

1. Flame test—The vapours emitted by substances at a high temperature impart characteristic colours to the non-luminous flame.

Heat a platinum wire in the flame. If the wire is clean, it becomes red hot without colouring the flame. In case the wire is not clean, clean it by repeatedly dipping it in concentrated hydrochloric acid and heating it in the flame. Now touch the paste made by moistening a little of the substance with concentrated HCl by the tip of the clean wire and hold this tip into the flame. Note the colour in the flame, if any. Now see the colour of the flame through a blue glass when a further clue is obtained regarding the element present.

In the following table, the colours of the flames as seen directly and also as seen through a blue glass are given.

Elements	*Flame colour*	*Flame colour through blue glass*
Sodium	golden yellow	not visible
Potassium	violet	violet red
Calcium	dull red	greenish grey.
Strontium	crimson	purple.
Barium	yellow green	blue green.
Borate	green	...
Copper	green with blue centre	...

If the flame is seen through two blue glasses (one over the other), instead of one, all flames except potassium are masked. Thus potassium can easily be detected in presence of others.

In the presence of the Second Group elements, the flame test should not be applied to the mixture as elements like lead and arsenic attack the platinum wire.

2. **Bead test**—The test consists in heating the substance under examination on a borax bead in the loop of a platinum wire. A loop is made at the end of the platinum wire and heated in the flame. The red hot wire is now dipped into borax when a trace of it adheres to the loop. On heating, this swells up and gives a clear transparent bead. The substance under examination is now touched with this bead and heated both in the oxidising and the reducing flames. The bead develops characteristic colours depending upon the nature of the substance under examination. *Only coloured oxides impart characteristic colours to the borax bead.*

Borax when heated is converted into sodium metaborate, boric anhydride and water.

$$Na_2B_4O_7.\ 10H_2O = 2NaBO_2 + B_2O_3 + 10H_2O.$$

The oxides of the metals under examination react with metaborate and boric anhydride giving ortho— and metaborates respectively. Thus with nickel salts, we get:

$$NiO + NaBO_2 = NiNaBO_3 \text{(orthoborate)},$$
$$NiO + B_2O_3 = NiO.\ B_2O_3 = Ni(BO_2)_2 \text{(metaborate)}.$$

The characteristic colours imparted to the borax bead by various metals when heated in the oxidising and reducing flames are given below:—

Metal	*Oxidising (nonluminous) flame*	*Reducing (luminous) flame*
Copper	Green when hot, blue when cold.	Red.
Iron	Yellow when hot, bottle-green when cold.	Same as in oxidising flame.
Chromium	Green.	Green.
Manganese	Amethyst-violet.	Colourless.
Cobalt	Sapphire blue.	Same as in oxidising flame.
Nickel	Yellow-brown.	Yellow-brown or grey.

3. **Charcoal test**—This test is given by a number of solids but it serves as a very good confirmatory test in case of Zn, Al, Sn and Mg. Mix a little of the precipitate to be tested for these elements with sodium carbonate and heat it in a charcoal cavity with reducing flame. Now moisten it with a few drops of cobalt nitrate solution and heat it in the oxidising flame.

Observation	*Inference*
Bright green mass	Zinc.
Dirty blue green mass	Tin.
Pink mass	Magnesium.
Blue mass	Aluminium or phosphate.

4. **Glow test for tin**—Take a portion of the mixture or precipitate to be tested for tin in a beaker or porcelain dish. Add to it about 3 ml. of concentrated HCl and a piece of zinc (tin free). Shake the whole thing together by means of a test tube half-filled with water and then put the test tube in the flame. A blue flame-mantle round the bottom of the test tube shows *tin*.

Other Preliminary Dry Tests.

Heat a small portion of the dried powder in an ignition tube:

(*a*) If chars ... organic matter.

(*b*) If melts ... fusible salts (alkali salts).

(*c*) If swells ... alums and borax.

(*d*) If changes colour on heating the dried powder:

Cold	*Hot*	*Inference*
Light yellow	Yellowish-brown	SnO_2.
White	Yellow	ZnO.
Yellow	Fuses brown	PbO.
Yellow	Orange	Bi_2O_3.
Red	Black	HgO, Pb_3O_4.

(*e*) If gases are evolved, when the powder is heated :—

Brown gas	Oxides of nitrogen from nitrates and nitrites, bromides, chromyl chloride.
Greenish yellow gas	Chlorine from chloride.
Violet	Iodine from iodide.
Smelling SO_2	Sulphite, thiosulphate.
Colourless turning lime water milky	Carbonate, oxalate.
Ammoniacal	Ammonium salt.
Vinegar smell	Acetate.
H_2S smell	Sulphide.

SECTION II

Separation of Insoluble Portion from Soluble

A given mixture may contain such ingredients as may not be all soluble in water, or ordinary acids. An insoluble substance for the purpose of qualitative analysis is defined as the one which does not dissolve in water, dilute and strong hydrochloric acids or nitric acid in cold or on boiling. But mostly for all practical purposes, the portion insoluble in water, and in dilute and concentrated hydrochloric acid is taken to be insoluble. A few exceptional cases will be referred to elsewhere.

Preparation of the Solution

The first important point in the analysis of a mixture for basic radicals is the preparation of its solution. There are a number of reagents in which the solution can be prepared, and in order to find out which one would be suitable for a particular mixture, take about 0·1 gram of the mixture and treat it with various reagents as follows:

(*i*) **Water**—Take about 0·1 gram of the mixture and treat it with about 5 ml. of water in cold; if it does not dissolve, then boil. If the mixture dissolves, take a gram of the mixture, dissolve and proceed on with the regular analysis.

(*ii*) *Dilute nitric acid*—Treat about 0·1 gram of the mixture with dilute nitric acid, warm and filter. To the filtrate, add dilute hydrochloric acid. If no precipitate is obtained, the First Group salts are absent and dilute nitric acid should not be used for preparing the solution. If, however, a precipitate is obtained, the presence of the First Group salts is indicated. In that case, treat about 1 gram of the mixture with dilute nitric acid, filter and proceed with the filtrate for the group analysis.

Mixture (1 g.)

Treat with dil. nitric acid, warm and filter.

Residue — Treat with strong HCl

- Residue Insoluble
- Filtrate

Filtrate — Add HCl (dil.) and filter.

- Precipitate Ag group
- Filtrate

Filtrate (from residue) and Filtrate (from Ag group): Mix.

Pass H_2S, and proceed with the regular analysis.

(*iii*) *Dilute hydrochloric acid*—If the mixture is insoluble in water and the First Group is also absent as tested above, treat about 0·1 gram of the mixture with dilute hydrochloric acid and boil. If it dissolves, prepare a solution of about 1 gram of the mixture and proceed on with the regular analysis.

(*iv*) *Concentrated hydrochloric acid*—If the First Group is absent and the mixture is insoluble in dilute hydrochloric acid as seen above.

treat about 1 gram of the mixture with about 5 ml. of concentrated hydrochloric acid, boil for about a minute and filter. If a white residue is left, it should be ordinarily treated as "insoluble".

(*v*) *Concentrated nitric acid*—It should be tried only in exceptional cases; *i. e.*, when the residue left undissolved in concentrated hydrochloric acid is coloured. The substances which do not dissolve in strong hydrochloric acid, but may dissolve in strong nitric acid are sulphides of copper, lead, bismuth, arsenic, cobalt and nickel. But they are rarely given. If the insoluble portion is coloured and is suspected to be mercuric sulphide (black), chromium oxide and chromic oxide (reddish-brown) or silver bromide or iodide (yellow), it is not necessary to use nitric acid.

If nitric acid has been at all used for preparing the solution, the soluble portion may be evaporated to a small bulk and then dissolved in hydrochloric acid (or neutralised with ammonium hydroxide, and just acidified with hydrochloric acid).

The use of nitric acid should be avoided as far as possible because it reacts with hydrogen sulphide in the Second Group, precipitates sulphur and creates difficulties.

"Insoluble" and the First Group both present—Treat the mixture as shown in the chart in (*ii*).

PRECAUTIONS—An excessive amount of the reagent should not be used in the preparation of solution. For dissolving about a gram of the mixture, one should not use more than 15 ml. of the dilute or 5 ml. of concentrated acids. If the acids have been added in large excess, it would mean an increased bulk in the subsequent groups and a waste of acids and other reagents.

SECTION III

First Group or Silver Group

Add a few drops of dilute hydrochloric acid to the *cold* solution of the mixture, prepared in water or dilute nitric acid. If a precipitate is produced, add more hydrochloric acid, till no more of the precipitate is formed. Filter the precipitate and wash it with cold water. Keep the filtrate for the analysis of the subsequent groups.

The precipitate may be of $PbCl_2$, Hg_2Cl_2 and $AgCl$. Boil the precipitate with water, and filter quickly, while hot.

<table>
<tr><td rowspan="2">Filtrate Test Pb.
White shining crystals separate on cooling—LEAD
(i) To a portion of the hot solution, add acetic acid and potassium chromate : a yellow ppt.—LEAD
(ii) To another portion of the hot sol., add potassium iodide : yellow ppt.—LEAD</td><td colspan="2">Residue
Test for Hg (ous) and Ag. Shake the residue with ammonium hydroxide, and filter.</td></tr>
<tr><td>Filtrate
Test for Ag; acidify with dil. nitric acid: a white ppt.—SILVER</td><td>Residue
If Black—MERCURY. Confirm with $SnCl_2$ test.</td></tr>
</table>

Second Group of Copper-Arsenic Group

Boil the filtrate of the First Group, and pass hydrogen sulphide to a small portion in a test tube. If no precipitate appears, dilute it and pass hydrogen sulphide again. If even now, no precipitate appears, the Second Group is taken to be absent and hydrogen sulphide should not be passed through the entire solution. If, however, a precipitate is obtained on passing hydrogen sulphide to the hot or the diluted solution, boil the whole solution, and pass hydrogen sulphide through it till saturation. Filter, the precipitate, dilute the solution and pass hydrogen sulphide again. Repeat the process till the precipitation is complete. Filter the precipitates for the Copper-Arsenic Group.

Wash the precipitate with hot water, and shake it with about 10 ml. of *yellow ammonium sulphide*, and filter. Test the residue on filter paper for the Copper Group, and the filtrate for the Arsenic Group, if a *permanent* yellow or brownish precipitate (but *not white*) is obtained on adding dilute hydrochloric acid *in excess* to the filtrate.

Copper Group

Take the residue insoluble in yellow ammonium sulphide, wash with hot water, and boil it with 4 ml. of 33% nitric acid (1 part of concentrated nitric acid, diluted with 2 parts of water), then filter.

Residue:— Black : HgS or S. Dissolve in aqua regia, dilute and filter.	*Solution*—To a small portion of the solution in test tube, add dilute sulphuric acid and alcohol. If no ppt. do not add sulphuric acid and alcohol to the whole solution, as Pb is absent. But if white ppt., add dil. sulphuric acid and alcohol to whole solution, and filter.

<table>
<tr>
<td rowspan="2">Divide the filtrate in two parts : (i) Add a clear copper foil : a grey deposit on copper. Hg.
(ii) Add $SnCl_2$: a white ppt. turning greyish MERCURY.</td>
<td rowspan="2">Precipitate. White : Pb. To it add a conc. sol. of ammonium acetate and filter; add acetic acid and pot. chromate to the filtrate : a yellow ppt.—LEAD.</td>
<td colspan="2">Filtrate—Boil off alcohol and add excess of ammonium hydroxide, and filter.</td>
</tr>
<tr>
<td>Precipitate. White : Bi (or Pb.) Confirm Bi by dissolving the ppt. in a few drops of conc. HCl, and diluting the sol. largely : white ppt.—BISMUTH. Confirm by stannite test. ($SnCl_2$+NaOH+Bi ppt : black mass).</td>
<td>Filtrate.—Cu and Cd. If the sol. is colourless, Cu absent and Cd tested by passing hydrogen sulphide :yellow ppt. If the sol. is blue in colour test for Cd and Cu both. (Cu is confirmed by adding acetic acid in excess, and then pot. ferrocyanide : a red ppt. —COPPER Acidify the blue sol. with an excess of conc. HCl, and pass hydrogen sulphide. Filter off the black ppt. of CuS, dilute the filtrate largely, and pass hydrogen sulphide again : a yellow ppt.—CADMIUM</td>
</tr>
</table>

If Arsenic Group is present, take whole of the yellow ammonium sulphide filtrate, precipitate completely with dil. HCl in excess, and filter. Reject the filtrate and boil the ppt. with about 10. ml. of conc. HCl and filter.

<table>
<tr>
<td rowspan="2">Residue.
Yellow
As or S :
Boil the residue with 3 ml. conc. HNO_3, dilute and filter. To the filtrate, add ammonium molybdate, and heat : yellow ppt.—ARSENIC.</td>
<td colspan="2">Filtrate—Boil the solution to drive off H_2S and divide the solution into two parts :
(i) To one part—add 2 iron nails, and boil, and filter. To the filtrate add $HgCl_2$ if white or greyish ppt.—TIN (Sb ppted. in black scales).
(ii) To the other part—introduce a piece of zinc in a platinum wire loop: black deposit on Pt.—ANTIMONY.
Alternate—for Sn and Sb.
Add ammonium hydroxide to the filtrate, till the solution is just alkaline; now add 5 g. solid oxalic acid, and boil, and pass hydrogen sulphide and filter.</td>
</tr>
<tr>
<td>Precipitate.
Orange
ANTIMONY.</td>
<td>Filtrate—Make the solution just alkaline with ammonium hydroxide, add acetic acid, till the solution is just acidic, boil and pass hydrogen sulphide : brownish yellow ppt.—TIN.</td>
</tr>
</table>

Third Group

Boil off hydrogen sulphide completely (test with lead acetate paper for this) from the filtrate of the Second Group and concentrate it to about 10 ml. Add about 1 ml. of concentrated nitric acid and boil. Test a little of the solution for *phosphate* by boiling with ammonium molybdate and also for *iron* in another portion by adding potassium ferrocyanide. Now add about 10 ml. of ammonium chloride solution and then ammonium hydroxide till the solution distinctly smells of ammonia.

Four types of cases may arise in the case of the Third Group analysis : (i) when no interfering acid radical, like phosphate, oxalate or fluoride be present; (ii) when oxalate be present; (*iii*) when fluoride or borate be present; and (iv) when phosphate be present. In the B.Sc. classes, we generally do not give two

*Sometimes, the residue of arsenic sulphide, especially As_2S_5, dissolves with difficulty in conc. HNO_3. In such cases heat the residue with 15 ml. of 6*N*—HCl and add powdered $KClO_3$ from time to time in small portions. When all the yellow sulphide has dissolved, dilute somewhat and filter off the residual sulphur. Evaporate the filtrate to 2 ml., add 2 ml. conc. HNO_3 and boil and add an excess of ammonium molybdate solution. Again boil. Yellow ppt.—As.

interfering acids together. But if at all more than one interfering acid be given, fluoride is eliminated first, then the oxalate, and lastly the phosphate.

Case I—*When the mixture does not contain any interfering acid.*

The precipitate obtained by adding ammonium chloride and ammonia to the filtrate of the Second Group (after removing hydrogen sulphide, and oxidising ferrous iron to ferric by nitric acid) may consist of the hydroxides of *iron*, *chromium* and *aluminium* and sometimes of *manganese*.

Filter the precipitate, wash it with water and boil the precipitate with a solution of caustic soda; when the vapours do not smell of ammonia, *i.e.*, all the ammonium salts have been decomposed, add a further quantity of caustic soda and an excess of a strong solution of bromine water (*sodium peroxide* may be used in place of bromine water), boil and filter.

<table>
<tr><td colspan="2">Residue—
May be iron or manganese. Boil with dil. nitric acid and filter.</td><td colspan="2">Solution—
Boil off excess of Br_2, and divide the solution in two parts if the solution is yellow. If the solution is not yellow, test only for Al.</td></tr>
<tr><td>Residue—
Manganese.
(i) Apply borax bead test. Amethyst bead :Mn.
(ii) Fuse with sod. carbonate and pot. nitrate : green mass which dissolves with pink colour in dil.H_2SO_4 .—MANGANESE</td><td>Solution—
Iron. Add. pot. ferrocyanide to this. Prussian blue colour, —IRON</td><td>Part I
If yellow—
Add excess of acetic acid till the alkali is neutralised and there is a distinct smell of acetic acid; and add lead acetate sol. : yellow ppt.—CHROMIUM.</td><td>Part II
Acidify the solution with nitric acid and then add ammonium hydroxide in excess, warm : a white gel. ppt.—ALUMINIUM Confirm by charcoal test.
Alternatively—
Boil the part II with an equal vol. of ammonium chloride sol.: white gel. ppt.—Al present.</td></tr>
</table>

Case II—*When fluoride is present as an interfering acid*—Take the precipitate of the Third Group as obtained above in a procelain dish, and add about 2 ml. of concentrated hydrochloric acid, and evaporate to dryness (stir with the glass rod to prevent spurting). Add about 2 ml. more of the acid, and repeat the process. The precipitate ought to be thus digested with HCl three or four times. Extract the residue with dilute hydrochloric acid (neglect the insoluble if any), add ammonium chloride and ammonium hyd-droxide and filter off the precipitate if any. Test the precipitate for the members of the Third Group as in case I, and mix the filtrate obtained at this stage with the original filtrates of the Third Group, and proceed with the mixed filtrate for the subsequent groups.

Case III—*When oxalate (or some other organic matter) is present as an interfering acid*—Take the precipitate of the Third Group as ob tained above on a precelain piece and ignite it for about 15 minutes. The oxalate is decomposed to carbonate or oxide. Dissolve the ignited mass as far as possible in dilute hydrochloric acid. Add ammonium chloride and ammonia to the solution. Test the precipitate thus obtained for the Iron Group as described in the case I, and mix the filtrate at this stage with the filtrate of the original Third Group and proceed on with the mixed filtrate for the subsequent groups.

Alternative Method for the Removal of Oxalates

To the precipitate of the Third Group, add concentrated nitric acid, and add to the solution a few crystals of potas sium chlorate and boil. The oxalates will be decomposed. To the solution, add ammonium chloride and ammonium hydroxide and test the precipitate for the Third Group as in case I. The filtrate obtained at this stage is mixed with the original filtrate of the Third Group and tested for the subsequent groups.

Case IV—*When phosphate is present as an interfering acid*—To the filtrate of the Second Group, add nitric acid, after the removal of hydrogen sulphide, and heat. In a portion of the solution, test for iron by adding potassium ferrocyanide (Prussian blue colour). To the rest of the solution, add ammonium chloride and an excess of ammonium hydroxide. The precipitate thus obtained would consist of the hydrous oxides or phosphates of the metals of Iron Group, as well as the phosphates of some of the subsequent groups. It is not necessary to filter at this stage. Add about 10 ml. of sodium acetate solution and then an excess of acetic acid till the

smell of ammonia is permanently replaced by that of vinegar. If the whole precipitate dissolves, then the Iron Group is usually absent. If a portion of the precipitate remains undissolved, it may be filtered out and tested for iron, chromium and aluminium as in the case 1 (phosphates also behaving as if they are oxides for the subsequent reactions); and the filtrate at this stage may be subjected to the method of the removal of phosphates (by adding ferric chloride etc.).

For a *rigorous* treatment the following procedure may be adopted. To the mixture obtained above after adding sodium acetate and acetic acid* add ferric chloride solution drop by drop* with constant stirring till the solution acquires a light red colour (the colour of the prepared tea); excess of ferric chloride should not be added as it further peptises the ferric phosphate precipitate to almost a clear solution. Boil for about 5 minutes and filter. The precipitate should be tested for the Iron Group (chromium and aluminium only; the iron has been initially tested). To the filtrate, add ammonium hydroxide, boil and *filter* off the excess of iron, and test the filtrate for the subsequent groups.

Fourth Group or Zinc Group

Warm the filtrate of the Third Group, and pass hydrogen sulphide in a portion of the solution till the solution smells of the gas. If a precipitate is obtained, pass the gas through the whole filtrate of the Iron Group. Filter off the precipitate, wash it and test it for the Zinc Group (Co, Ni, Zn and Mn) as follows, and keep the filtrate for the subsequent groups.

Shake the precipitate with dilute hydrochloric acid in cold and filter :

*Sometimes the given mixture contains a quantity of iron sufficient to precipitate the phosphates completely. In that case we get a red coloured solution on the addition of sodium acetate and acetic acid. In this case it is not necessary to add any quantity of ferric chloride to eliminate phosphates.

<table>
<tr>
<td rowspan="2">Residue—
Black—
Ni and Co.*
Take a portion of the residue and heat it with about 1 ml. conc. HCl and a few crystals of potassium chlorate. Filter and evaporate the solution to almost dryness in a dish. Dissolve the residue in water, cool; add sodium bicarbonate till it is in sufficient excess. Now add bromine water. Cool and shake for sometime.—
(i) Apple green colour in cold and no change on heating—COBALT.
(ii) Apple green colour in cold and blackening on heating—Co and Ni both.
(iii) No green colour in cold but blackening on heating—NICKEL only.
Borax bead tests—If Co—blue which also masks the colour of nickel bead. If Co absent nickel gives brown bead.</td>
<td colspan="2">Solution—Boil off hydrogen sulphide (test with lead acetate paper) if any; add an excess of caustic soda; boil and filter;</td>
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<td>Residue—
Mn.
Fuse a portion with sod. carbonate and pot. nitrate or pot. chlorate; a green mass, which dissolves to a pink sol. in water—
MANGANESE
Confirm by the borax bead test —amethyst.</td>
<td>Solution—
Zn.
Pass hydrogen sulphide;
white ppt.—
Zn.
Confirm by charcoal test with Co nitrate; bright green—
ZINC.</td>
</tr>
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APPENDIX

Mixed precipitation of the Third and Fourth Groups—
An alternate method.

If manganese and cobalt are present in the mixture in excess, sometimes they may be precipitated in the Third Group and cause difficulty. In that case, the Third and Fourth Groups should be precipitated together and analysed as shown below. But in practice this rarely happens and it is no good, adding, one more long group of seven metals (Fe, Cr, Al, Co, Ni, Mn and Zn) after a long Second Group. It is advisable to precipitate Third and Fourth Groups separately.

Take the filtrate of the Second Group, and concentrate to about 20 ml. Add ammonium chloride and then ammonium hydroxide in excess, and pass hydrogen sulphide in excess. Filter and wash the precipitate. Test the precipitate for Fe, Cr, Al, Ni, Co, Mn and Zn as shown below. Keep the filtrate for boiling in order to drive off H_2S and to concentrate it for the subsequent groups.

Treat the precipitate with dilute hydrochloric acid, shake for two or three minutes and filter.

*For the potassium cyanide test, see the reactions.

smell of ammonia is permanently replaced by that of vinegar. If the whole precipitate dissolves, then the Iron Group is usually absent. If a portion of the precipitate remains undissolved, it may be filtered out and tested for iron, chromium and aluminium as in the case 1 (phosphates also behaving as if they are oxides for the subsequent reactions); and the filtrate at this stage may be subjected to the method of the removal of phosphates (by adding ferric chloride etc.).

For a *rigorous* treatment the following procedure may be adopted. To the mixture obtained above after adding sodium acetate and acetic acid* add ferric chloride solution drop by drop* with constant stirring till the solution acquires a light red colour (the colour of the prepared tea); excess of ferric chloride should not be added as it further peptises the ferric phosphate precipitate to almost a clear solution. Boil for about 5 minutes and filter. The precipitate should be tested for the Iron Group (chromium and aluminium only; the iron has been initially tested). To the filtrate, add ammonium hydroxide, boil and *filter* off the excess of iron, and test the filtrate for the subsequent groups.

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Warm the filtrate of the Third Group, and pass hydrogen sulphide in a portion of the solution till the solution smells of the gas. If a precipitate is obtained, pass the gas through the whole filtrate of the Iron Group. Filter off the precipitate, wash it and test it for the Zinc Group (Co, Ni, Zn and Mn) as follows, and keep the filtrate for the subsequent groups.

Shake the precipitate with dilute hydrochloric acid in cold and filter :

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Fuse a portion with sod. carbonate and pot. nitrate or pot. chlorate; a green mass, which dissolves to a pink sol. in water—MANGANESE Confirm by the borax bead test —amethyst.</td>
<td>Solution—
Zn.
Pass hydrogen sulphide; white ppt.—
Zn.
Confirm by charcoal test with Co nitrate; bright green—ZINC.</td>
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APPENDIX

Mixed precipitation of the Third and Fourth Groups—An alternate method.

If manganese and cobalt are present in the mixture in excess, sometimes they may be precipitated in the Third Group and cause difficulty. In that case, the Third and Fourth Groups should be precipitated together and analysed as shown below. But in practice this rarely happens and it is no good, adding, one more long group of seven metals (Fe, Cr, Al, Co, Ni, Mn and Zn) after a long Second Group. It is advisable to precipitate Third and Fourth Groups separately.

Take the filtrate of the Second Group, and concentrate to about 20 ml. Add ammonium chloride and then ammonium hydroxide in excess, and pass hydrogen sulphide in excess. Filter and wash the precipitate. Test the precipitate for Fe, Cr, Al, Ni, Co, Mn and Zn as shown below. Keep the filtrate for boiling in order to drive off H_2S and to concentrate it for the subsequent groups.

Treat the precipitate with dilute hydrochloric acid, shake for two or three minutes and filter.

*For the potassium cyanide test, see the reactions.

Residue—Ni and Co. Test as in Group IV.	*Solution*:—Boil to drive off H_2S, cool, and add caustic soda and bromine water (or sodium peroxide) boil and filter.

Residue—Iron and Manganese. Boil with dil. HNO_3 a minute and filter	*Solution*—Chromium, aluminium and zinc. Boil off bromine and divide into 2 parts.

		I	II
Residue *Mn.* (1) Bead test. (2) Fuse with Na_2CO_3 and $KClO_3$ or KNO_3 in the loop of platinum wire : a green mass. MANGANESE.	*Solution*—*Fe.* Add $K_4Fe(CN)_6$: deep blue colour confirms IRON	Acidify with excess of acetic acid and add lead acetate: a yellow precipitate—CHROMIUM	Acidify with dil. nitric acid and add NH_4OH, boil and allow to stand: a white gelatinous precipitate. ALUMINIUM (confirm by charcoal test). Pass H_2S through the filtrate : a white precipitate—ZINC. (Confirm by charcoal test)

Fifth Group or Calcium Group

Boil off H_2S from the filtrate of the Fourth Group; concentrate it to about 50 ml., boil add 2 to 3 ml. of ammonium hydroxide and ammonium carbonate in slight excess. Allow the mixture to stand for about five minutes and then filter the precipitate if any. Washit with water and test it for barium, strontium and calcium. Keep the filtrate for testing magnesium.

Dissolve the precipitate of the Fifth Group in acetic acid. To a few ml. of this in a test tube, add potassium chromate solution. If a precipitate is obtained, this shows that barium is present. Then add K_2CrO_4 to the entire solution and filter.

<table>
<tr>
<td rowspan="2">Precipitate—yellow
BARIUM.
Perform flame test with the precipitate : a persistent green flame.</td>
<td colspan="2">Solution—Add ammonium sulphate solution in excess, heat, scratch the sides, and allow to stand. Filter the precipitate if any.</td>
</tr>
<tr>
<td>Precipitate
STRONTIUM.
Perform flame test with the precipitate : persistent red.</td>
<td>Solution.—Add ammonium oxalate solution: a white precipitate shows CALCIUM.
Perform flame test with the precipitate : non-persistent red.</td>
</tr>
</table>

Sixth Group

To the filtrate of the Fifth Group, add a few ml. of ammonium oxalate solution, boil and filter off the precipitate if any. (This is done to remove calcium if passed over). Now add sodium phosphate solution to it : a white precipitate on shaking and scratching the sides of the test tube with a glass rod.—MAGNESIUM. Confirm by charcoal test; with cobalt nitrate solution : pink mass.

SODIUM, POTASSIUM AND AMMONIUM

Sodium—This is detected by flame test. A golden yellow flame not visible through a cobalt glass—Sodium.

Potassium—A violet flame. This colour is masked by the yellow colour of sodium. See through a cobalt glass. The sodium light is cut off and so potassium can be identified by its lilac flame. The best way of identifying potassium is to see its flame through two cobalt glasses one over the other.

Ammonium—Heat a portion of the original mixture with caustic soda solution : smell of ammonia gas shows the presence of AMMONIUM radical in the mixture.

SECTION IV

THE ACIDS

1. *To a small portion of the mixture, add dilute sulphuric acid and warm*

Observation	Inference	Confirmatory tests
(*a*) Effervescence in cold and evolution of CO_2 on warming.	Carbonate	Pass the gas evolved in lime water; it is turned milky.
(*b*) A colourless gas giving the smell of burning sulphur.	Sulphite	A filter paper dipped in $K_2Cr_2O_7$ solution is turned green on exposure to the gas.
(*c*) A colourless gas giving the smell of H_2S.	Sulphide	A filter paper dipped in lead acetate solution turns black on exposure to the gas.
(*d*) Light brown coloured fumes having pungent odour.	Nitrite	Moisten a filter paper with KI and starch and a few drops of dilute H_2SO_4 and expose to the gas; the paper turns blue.
(*e*) Smell of SO_2 and a white precipitate of sulphur.	Thiosulphate	

Heat a small amount of the mixture with strong sulphuric acid

Observation	Inference	Confirmatory tests
(*a*) A crackling sound accompanied with the evolution of yellow coloured gas.	Chlorate	
(*b*) Vapours having smell of vinegar.	Acetate	Extract small portion of the mixture with hot water, filter, cool and add $FeCl_3$: a blood red colour.
(*c*) Light brown vapours having pungent smell. The evolution of vapours increases on adding copper turnings.	Nitrate	1. To a solution of the mixture, add strong ferrous sulphate solution, shake and cool. Now add conc. H_2SO_4 cautiously from the sides drop by drop. A ring is produced at the junction of acid and the solution. (This test is not reliable if the mixture contains nitrite, bromide or iodide). 2. The brown fumes are insoluble in water; when they are passed through water, it is not coloured (distinction from bromide).
(*d*) Evolution of a mixture of CO and CO_2. The gas (CO)	Oxalate	Neutralise the sodium carbonate filtrate with excess of acetic acid.

(Continued)

Observation	Inference	Confirmatory tests—
burns with a blue flame and turns lime water milky (CO_2).		and add $CaCl_2$: a white precipitate which decolourises $KMnO_4$ solution on warming in presence of dilute sulphuric acid.
(*e*) White fumes with pungent odour. The evolution of fumes increases on adding MnO_2.	Chloride	Acidify the sodium carbonate filtrate with excess of nitric acid and add $AgNO_3$: a white precipitate soluble in NH_4OH (If Na_2CO_3 contains chloride as impurity, we shall get this test even if chloride is absent in the mixture. In that case, extract a small portion of the original mixture with warm dilute nitric acid, filter and add $AgNO_3$; a white precipitate soluble in NH_4OH shows chloride).
(*f*) Brown coloured vapours having smell of bromide.	Bromide	1. These fumes are soluble in water, giving yellow solution (distinction from nitrate): Add $AgNO_3$ to this solution; a yellow precipitate. 2. Acidify the sodium carbonate filtrate with excess of nitric acid; add $AgNO_3$; a yellow precipitate insoluble in NH_4OH.

(*Continued*)

Observation	Inference	Confirmatory tests
(*g*) Violet vapours with smell of iodine.	Iodide	Acidify the sodium carbonate filtrate with excess of nitric acid and add $AgNO_3$: a yellow precipitate insoluble in NH_4OH.

3. *Heat a portion of the mixture with concentrated sulphuric acid and sand in a test tube*—Oily drops appear in the test tube. Dip a glass rod in water and then expose it to the vapours ensuing from the test tube. If a white deposit on the rod—FLUORIDE. Neutralise a portion of the sodium carbonate filtrate with excess of acetic acid and add $CaCl_2$: a white precipitate which does not decolorise acidified potassium permanganate solution (distinction from oxalate).

4. *Treat a portion of the mixture with about 2 ml. of conc. H_2SO_4 and 3 ml. of ethyl alcohol in a porcelain dish*—Stir the whole mass with glass rod and apply flame: if it burns with a green flame—BORATE. (This test is not reliable in the presence of copper in a mixture. In that case, the test for borate should be done with calcium fluoride.)

5. *Heat a portion of the mixture with about 3 ml. of conc. nitric acid (filter if the whole thing does not dissolve). Now add to it ammonium molybdate and boil again*—A canary yellow precipitate or colour shows the presence of PHOSPHATE, or ARSENIC. Repeat this test with the filtrate of the Second Group. A yellow precipitate shows PHOSPHATE.

6. *Tests with sodium carbonate filtrate*—Boil about 0·5 gram of the salt mixture with about two grams of sodium carbonate and 20 ml. of distilled water for about ten minutes. Filter and test the filtrate as follows:—

(*a*) Acidify a portion of the filtrate with an *excess* of hydrochloric acid and add $BaCl_2$: a white precipitate, insoluble in nitric acid, shows SULPHATE.

Filter off the precipitate and add bromine water to the filtrate: a white precipitate is again formed—SULPHITE.

(*b*) Acidify another portion of the filtrate with nitric acid in *excess* and add $AgNO_3$ solution :

(*i*) a white precipitate shows chloride;

(*ii*) a yellow precipitate—may be a mixture of chloride, bromide and iodide.

(*c*) Acidify a third portion with an *excess* of acetic acid and add $CaCl_2$ solution : a white precipitate shows fluoride or oxalate.

Treat the precipitate with dilute $KMnO_4$ solution in presence of dilute sulphuric acid and warm.

(*i*) The colour of $KMnO_4$ is discharged—oxalate.

(*ii*) The colour of $KMnO_4$ is not discharged —fluoride.

Combinations of acids

Sometimes if certain acid radicals occur together, it becomes difficult to test one in presence of the other. Such cases are:

(1) Carbonate and oxalate.

(2) Chloride, bromide and iodide.

(3) Sulphide, sulphite, sulphate, and thiosulphate.

(4) Nitrite and nitrate.

(5) Nitrate and bromide.

(6) Nitrate and iodide.

The methods adopted in testing for one in presence of the other are as follows:—

(1) *Carbonate and oxalate*—When they occur together in a mixture, it becomes difficult to test for oxalate. On adding dilute sulphuric acid, we get the effervescence of CO_2 which shows the presence of carbonate; but when concentrated H_2SO_4 is added we again get CO_2 and we cannot say whether it has come from the decomposition of carbonate or oxalate. They are tested as follows:—

Heat a portion of the mixture with dilute sulphuric acid; evolution of CO_2 gas shows the presence of carbonate because oxalate will not be decomposed by dilute H_2SO_4. Add the dilute acid in excess, till no more of the effervescence, and warm. Now add a pinch of manganese dioxide . If fresh effervescence ensues, the oxalate is also present.

This can also be confirmed by adding $CaCl_2$ to a portion of the sodium carbonate filtrate, acidified with an excess of acetic acid when a white precipitate will be obtained which will decolorise potassium permanganate solution in presence of dilute H_2SO_4.

(2) *Chloride, bromide and iodide*—When all the three or even two are present together, the colour of the vapours obtained on heating a portion of the mixture with concentrated H_2SO_4 cannot give us a sure indication, as the colour of chlorine will be masked by that of bromine or iodine. Again, when we add $AgNO_3$ to the sodium carbonate filtrate acidified with HNO_3 and get a yellow precipitate, we cannot say whether chloride is present or not, as the yellow colour of AgBr or AgI will mask the white colour of AgCl.

In such a case, they are tested as follows:—

Take about 10 ml. of sodium carbonate filtrate in a beaker, add excess of dilute H_2SO_4 and then sodium nitrite gradually. On heating, vapours of iodine pass out. Continue heating and adding $NaNO_2$ till the entire iodine is driven out. This is indicated by the colour of solution changing from dark violet to colourless. [The colour of iodine vapours should not be confused with that of NO_2 vapours obtained by the action of dilute H_2SO_4 on $NaNO_2$, the former are violet while the latter are light brown.] Now make the solution alkaline with carbonate to fix up HBr and add concentrated nitric acid. The solution again gets coloured if bromide is present and bromine fumes are evolved. Go on heating and adding nitric acid gradually till the entire bromine is evolved and the solution again becomes colourless. Now add $AgNO_3$; the formation of white precipitate shows the presence of chloride. Thus, one can find out whether the three or two or only one are present.

An alternative method—Take a few drops of the mixed solution in a test tube, add a few drops of chloroform and then chlorine water, drop by drop, and shake after each addition.

(*i*) If the chloroform not coloured:—bromide and iodide both absent. Acidify another part of the solution with nitric acid and test for chloride with silver nitrate (a white precipitate indicates the presence of chloride).

(*ii*) If the chloroform is at once coloured brown:—*bromide* present, and iodide absent; chloride may also be present.

(*iii*) If the chloroform is coloured violet:—*iodide* is present, and bromide and chloride may also be present.

(*iv*) If iodide is present, add more of chlorine water drop by drop, and shake. If the violet colour disappears (iodine would change to iodate), and the chloroform assumes brown colour, then bromide is also present. If no brown colour, then bromide is absent.

If iodide and bromide are both present, they are to be decomposed before one can test for chloride. This may be done in two ways: (*i*) Heat the original mixture with concentrated nitric acid,

till iodine and bromine fumes are completely driven off. (*ii*) Acidify a portion of the mixed solution with dilute sulphuric acid and add a little potassium permanganate and boil in a porcelain dish, till the brown colour of the solution disappears. Add more of permanganate and boil and repeat the process 3-4 times, until permanganate no longer gives brown colour. Now the mixture is free from bromide and iodide. Acidify with nitric acid and add silver nitrate. A white precipitate indicates the presence of *cholride.*

(3) *Cyanide and chloride*—Both of them give a white precipitate with silver nitrate, soluble in ammonium hydroxide and insoluble in nitric acid. Cyanides may be distinguished from chlorides by the evolution of carbon monoxide when treated with strong sulphuric acid, and by the Prussian blue test—(add caustic soda to a soluble salt, and a few drops of ferric chloride solution, boil and acidify with hydrochloric acid; a Prussian blue colour or precipitate would indicate *cyanide*).

If both are present, boil the mixed solution with an excess of concentrated nitric acid for 5 minutes. Hydrocyanic acid will be removed. Now test for chloride with silver nitrate. A white precipitate indicates *chloride.*

(4) *Sulphide, sulphite, sulphate and thiosulphate*—Take the sodium carbonate filtrate and follow the following scheme:

Na_2S, Na_2SO_3, Na_2SO_4 and $Na_2S_2O_3$.
Shake with $PbCO_3$ and filter.

Residue
PbS (black)
SULPHIDE

Filtrate
Add $BaCl_2$ in-
excess and filter.—

Residue
Sulphide and
Sulphate
Acidify with excess
HCl and filter.

Filtrate
Thiosulphate
Acidify with
HCl excess.
White ppt. of S
and smell of SO_2.
THIOSULPHATE

Residue
white
SULPHITE

Filtrate
Sulphite-
Add Br_2 water
and shake.
A white ppt.
SULPHATE

(5) *Sulphide, sulphite* and *sulphate*—When the mixture is treated with dilute sulphuric acid, it becomes difficult to identify sulphide (if both are present together) only by the smell of the gases. If such a case is suspected, proceed as follows:—

Shake about 10 ml. of the sodium carbonate filtrate with solid lead carbonate. In presence of sulphide, the colour of white carbonate will change to black, due to the formation of lead sulphide. Filter off the insoluble portion Remove whole of the sulphide in this way. Now acidify the solution with concentrated HCl and add $BaCl_2$: a white precipitate will be obtained if sulphate is present. Filter off the precipitate if any and add bromine water to the solution: the formation of a white precipitate again shows the presence of sulphite.

(6) *Nitrite and nitrate*—If nitrite is present in the mixture, it is not possible to test for nitrate by heating the mixture with concentrated sulphuric acid and copper turnings, or by the ring test because in both cases, nitrite will interfere. They may be tested as follows:—

Test for nitrite with dilute sulphuric acid (nitrate will not interfere) and confirm its presence by exposing a filter paper dipped in KI, starch and dilute H_2SO_4 to its vapours, when the paper turns blue.

Now boil a portion of the sodium carbonate filtrate with ammonium chloride (solid), or urea and dilute sulphuric acid. Thus nitrite is decomposed. When the whole of nitrite is decomposed (no test given with paper dipped in KI, starch and dilute H_2SO_4), add to it zinc and dilute H_2SO_4 and boil. The nitrate is thus reduced to nitrite and again we shall get the test for nitrite with paper dipped in KI, starch and dilute H_2SO_4. Thus nitrate may be tested in presence of nitrite.

(7) *Nitrate and bromide or iodide*—From the colour of the vapours obtained on heating the mixture with concentrated H_2SO_4, it is difficult to say whether they are present together or singly. They can, however, be tested as follows:—

(*a*) *Nitrate and bromide*—Take about 10 ml. of the sodium carbonate filtrate, acidify it with dilute H_2SO_4 and add zinc and warm. Nitrate is thus reduced to nitrite (bromide not effected) and can be tested with the help of a paper dipped in potassium iodide and starch. Having tested for nitrate, bromide can be tested as in (2).

Alternatively—Treat the acidified solution with a solution of silver sulphate. Bromide will be removed as silver bromide. Filter and test for nitrate in the filtrate.

(*b*) *Nitrate and iodide*—Acidify about 10 ml. of the sodium carbonate filtrate with dilute H_2SO_4 and heat it with some zinc. If only nitrate is present, it will be reduced to nitrite and will give test with KI and strach. If both nitrate and iodide are present, we shall get iodine liberated from iodide by nitrous acid formed. Thus we shall get blue colour with starch even without adding KI.

Alternatively—Treat the acidified solution with silver sulphate. Iodide is removed as silver iodide. Test for nitrate in the filtrate.

SECTION V

Examination of the Insoluble Substances.

The insoluble substances have been classified according to their colour. They are :

	Colour-	*Substance*
1.	White	$AgCl$, $BaSO_4$, $SrSO_4$, $PbSO_4$, CaF_2 (fluorspar), SnO_2, Sb_2O_4, Al_2O_3.
2.	Yellow	$AgBr$ and AgI.
3.	Green	Cr_2O_3 and $Cr_2(SO_4)_3$.
4.	Black	HgS.
5.	Violet	$CrCl_3$.

They can be tested as follows:—

1. *White*—(*a*) *AgCl*—(*i*) It dissolves in NH_4OH. Add dilute HNO_3 to this solution; the precipitate reappears.

(*ii*) The colour changes to violet on expsure to light.

(*iii*) Prepare sodium carbonate filtrate,* it will give the test for sulphide.

(*b*) $PbSO_4$—(*i*) Prepare sodium carbonate filtrate,*it will give the test for sulphate.

*Take about 0·2 g. of the insoluble and mix with 1 g. of Na_2CO_3 and 10 ml. of water. Boil for five minutes and filter. Neutralise the filtrate with an excess of dilute nitric acid and test for chloride with $AgNO_3$.

**Take about 0·2g of the insoluble residue and mix with 1 g. of Na_2CO_3 and 10 ml. of water. Boil for five minutes and filter. Neutralise the filtrate with an excess of dilute nitric or hydrochloric acid, and test for sulphate with $BaCl_2$.

ACID RADICALS

Reagent	Acetate	Borate	Bromide	Carbonate	Chlorate	Chloride	Fluoride	Iodide	Nitrite	Nitrate	Oxalate	Phosphate	Sulphate	Sulphide	Sulphate	Thiosulphate
1. Dilute H_2SO_4 warm	Vinegar smell	→		CO_2 effer. in cold.						brown fumes	$+MnO_2$ CO_2 effer.			H_2S smell.	SO_2 smell.	$S+SO_2$
2. Heat with conc.	"	+alcohol (burn)→ Green edged flame	$+MnO_2$ $\to Br_2$ (brown)	"	Cracking sound.	$+MnO_2\to$ Cl_2(yellow)	+Sand (On moist rod, white deposit)	$+MnO_2\to$ I_2 (violet)	+Cu turn. →brown fumes.	"	$CO+CO_2$			"	"	"
3. Excess of dil. HNO_3 $+Ag\ NO_3$			Light yellow ppt. insol. in NH_4OH.			Wihte ppt. sol. in NH_2OH-		Yellow ppt. sol. in NH_4OH.								
4. Special test.	Neutral soln. with $FeCl_3$ →red col.								Ring test with $FeSO_4$ $+H_2SO_4$ conc.	KI+dilute $H_2SO_4\to$ I_2; test with starch.	$CaCl_2\to$ white ppt. insol. in excess acetic acid.	Conc.-HNO_3 +Am. molby. (heat)→ Canary yellow ppt.	$BaCl_2\to$ White ppt. insol. in HNO_3 excess.	Test H_2S with Pb acetate paper →black.	Test SO_2 with K_2CrO_4 paper →green.	

Halogen Acids
$Cl'+Br'+I'$

(*a*) Add a few drops of $CHCl_3$ and chlorine water.
(i) $CHCl_3$ not coloured—Br' and I' bsent. Test for Cl'.
(ii) $CHCl_3$ brown—Br' presents I' absent; Cl' may also be present.
(iii) $CHCl_3$ violet—I' present. Add more Cl_2 water.
If now brown, Br' is also present.
(*b*) Add H_2SO_4 dil.+$NaNO_2$.
If violet fumes given, I' present. Add $NaNO_2$ till iodide removed. Conc. and add conc. HNO_3. —Brown fumes, Br'. Br', and add Ag NO_3—white ppt. Cl'.

Nitrite+Nitrate

Test for nitrite with KI+dil. H_2SO_4+starch solution (blue colour). Decompose nitrite completely by heating with NH_4Cl. Reduce NO_3' to NO_2 by Zn+dil. H_2SO_4 and test for NO_2' again.

Nitrate+Bromide

Test for with $AgNO_3'$. Reduce nitrate to NO_2' by Zn+dil H_2SO_4 and test for nitrate with KI+starch.

Oxalate+Carbonate

Decompose CO''_3 by adding excess of H_2SO_4 (dil). When no effer., add MnO_2. Fresh effer.→oxalate.

Sulphide+Sulphite+Sulphate+Thiosulhpate

Shake with $PlCO_3$ and filter.

Residue PbS (black) *Sulphide*

Filtrate: Add $BaCl_2$ in excess and filter.

Residue $SO_3''+SO_4''$ Acidify with excess HCl and filter.

Residue white *Sulphate*

Filtrate Add Br_5 water and shake; white ppt.—*Sulphite*

Filtrate—Acidify with HCl execess white ppt. of S $+SO_2$ smell. *Thiosulphate*.

Insoluble Residue

White—$BaSO_4'$ $PbSO_4'$ $SrSO_4'$ CaF_2, SnO_2, Sb_2O_4, Al_2O_3, AgCl
Yellow—Ag Br, Ag I; dark brown Fe_2O_3; green and violet Cr_2O_3, $Cr_2(SO_4)_3$, $CrCl_3$
Treat with aqua regia to change Ag Br and AgI to AgCl. Add ammonia and filter.

Filtrate AgCl which re-ppts. on adding HNO_3.

Residue Fuse with $Na_2CO_3OKNO_3$ mixture and boil with water and filter.

Residue Boil with HCl and filter

Residue Brown—Fe_2O_3.

Filtrate Ba", Pb", Sr", Test as in Group Analysis.

Filtrate—Silicate, aluminate, stanuate, antimoniate, arsenate, chromate. Divide into large and small portions.

Large portion Acidify and pass H_2S and test for Sn, As, and Sb in ppt. and evaporate the filtrate to dryness to remove silica and test for Al and Cr as in Fe Group.

Small portion Test for SO_4''. Evaporate and test for silica in the residue by CaF_2+conc. H_2SO_4.

*Insol. Sb_2O_4 and SnO_2 may be separately tested by fusing the residue with Na_2Co_3 and S The residue is treated with dil. HCl. H_2S smell is given out and As_2S_3 and Sb_2S_3 precipitated. Proceed as in Arsenic Group.

(*ii*) Heat a portion with a concentrated solution of ammonium acetate and acetic acid; it partly dissolves.

Now filter and add K_2CrO_4 solution to it; a yellow precipitate is obtained.

(*c*) *$BaSO_4$ and $SrSO_4$*—(*i*) Prepare sodium carbonate filtrate*; it will give the the test for sulphate.

(*ii*) Perform the flame test with the washed sodium carbonate residue and find out whether it is barium (green) or strontium (crimson).

(*iii*) The residue left in preparing the sodium carbonate filtrate should be treated with acetic acid and filtered. The filtrate can be tested for barium or strontium with potassium chromate or ammonium sulphate as in the Fifth Group.

(*d*) *CaF_2 (fluorspar)*—(*i*) Test for the fluoride with concentrated H_2SO_4 and sand.

(*ii*) To a portion of the insoluble residue, add concentrated H_2SO_4 and evaporate to dryness on a porcelain piece. This reaction should be performed in a *fuming cupboard only*. Do it repeatedly 3 or 4 times. Now the residue left will give flame test for calcium.

Alternatively—Heat a portion of the residue in a loop of platinum wire with concentrated sulphuric acid. Now, touch the residue with concentrated hydrochloric acid and apply flame test for calcium.

(*e*) *SnO_2* and *Sb_2O_3*—(*a*) Take a portion of the insoluble residue, mix it with an equal weight of Na_2CO_3 and twice its weight of sulphur and fuse it on a porcelain piece. As it is being heated, go on adding sulphur from time to time. Now treat the fused mass with water and add to it dilute HCl; (test for H_2S with lead acetate paper); an orange precipitate shows antimony, while a greyish-yellow precipitate shows tin.

(*b*) Stannic oxide may also be tested by fluorescent flame mantle test. (See *tin.*)

(*f*) Al_2O_3—Ignite a portion of the insoluble residue with sodium carbonate in a charcoal cavity. Cool and add to it a few drops of cobalt nitrate. Heat again. The formation of a blue mass shows the presence of aluminium.

2. *Yellow*—AgBr or AgI.

To portion of the insoluble residue, add zinc and dilute sulphuric acid and boil. AgBr and AgI are reduced to metallic silver which can be filtered off and washed. The filtrate is tested for bromide and iodide as usual. The residue can be tested for silver by dissolving it in nitric acid and adding dilute HCl, when a white precipitate is formed.

3. *Green*—Cr_2O_3—Fuse a portion of the insoluble salt with equal weights of Na_2CO_3 and KNO_3 (or $KClO_3$) on a porcelain piece, when a yellow mass is obtained. Dissolve it in water and add CH_3COOH and then lead acetate; a yellow precipitate is obtained.

4. *Violet*—$CrCl_3$—(1) Fuse a portion of the residue with equal weights of Na_2CO_3 and KNO_3 on a porcelain piece. Dissolve in water. Divide the solution into two portions: (*i*) add acetic acid and lead acetate to one portion: yellow precipitate is obtained—CHROMIUM. (*ii*) To another portion, add dilute nitric acid in *excess* and then silver nitrate. A white precipitate indicates CHLORIDE.

5. *Green*—$Cr_2(SO_4)_3$—Fuse a portion of the green residue with sodium carbonate and potassium nitrate on a porcelain piece. Dissolve the fused mass in water. Divide it into two portions: (*i*) To one portion, add acetic acid in excess, and lead acetate. A yellow precipitate indicates CHROMIUM. (*ii*) To another portion, add excess of dilute hydrochloric acid, and then barium chloride. A white precipitate indicates SULPHATE.

6. *Black*—HgS—Dissolve the residue in boiling aqua regia; dilute the solution and add stannous chloride: a white precipitate is obtained which turns grey on heating with excess of stannous chloride. The presence of MERCURY is thus indicated. Treat another portion of the residue with zinc and dilute sulphuric acid, hydrogen sulphide will evolve, which is tested with lead acetate paper. Black spot on the paper indicates SULPHIDE.

Insoluble Residue

(*t*) $BaSO_4$, $SrSO_4$, $PbSO_4$, (*ii*) AgCl, AgBr, AgI, (*iii*) SnO_2, Sb_2O_4, Al_2O_3, Fe_2O_3, (*iv*) $CrCl_3$, CaF_2 As_2S_3. Treat with aqua regia to change AgBr and AgI to AgCl. Add ammonia and filter.

<table>
<tr><td rowspan="3">Ftltrate: Ag Cl which reppts. on adding HNO_3. Test with Zn and H_2SO_4</td><td colspan="4">Residue : Fuse with $Na_2CO_3+KNO_3$ mixture and boil the product with water, and filter.</td></tr>
<tr><td colspan="2">Residue : Contains Fe_2O_3(brown), $BaCO_3SrCO_3$, $PbCO_3$, and unchanged SnO_2, CaF_2 etc. Boil with HCl and filter.</td><td colspan="2">Filtrate : Contains silicate aluminate, stannate, antimoniate, arsenate, chromate (yellow), sulphate and fluoride and excess of Na_2CO_3. Divide into a large and a small portion.</td></tr>
<tr><td>Residue ; Brown Fe_2O_3 ; confirm by borax bead.</td><td>Solution; Ba^{++},Pb^{++} Sr^{++}.Test as in the group analysis.</td><td>Large portion : Acidify and pass H_2S as in Second Group for Sn, As and Sb; evaporate the filtrate to dryness to remove silica and test for Al, and Cr in the 3rd Group.</td><td>Small portion : Test for SO_4^{--}. Evaporate and test the residue for silica by CaF_2 and H_2SO_4.</td></tr>
</table>

PART IV

SEMIMICRO ANALYSIS AND SPOT TESTS

Section I—General Instructions

The entire field of chemical analysis is nowadays divided into four groups in regards to the quantity one handles in the analysis:

Class	*Weight of solid analysed*	*Volume of solution analysed*
Macro: Grams	0·5 g to 0·2 g	more than 20-10 ml.
Semimicro: Centigram	0·2-0·02 g.	10-0·5 ml.
Micro : Milligram	2-0·1 mg	0·5 ml.-20 cu.mm.
Ultramicro : Microgram	10-0·1 μg	20-0·2 cu.mm.

Since the year 1929, Spot Analysis has been introduced in most of the institutions as the routine analysis in place of the usual macroanalysis. The technique of semimicro analysis and spot tests is simple and economical. Fiegl has been the pioneer in this work and he and his students have considerably elaborated this technique since 1918.

Most of the appliances used in semimicro analysis are miniatures of those used in macro analysis. The exception is the *hand centrifuge* which can be easily procured and the centrifuge tubes can be blown by local glass blowers.

Test-tubes and Centrifuge Tubes. Small pyrex test-tubes (75×10 mm., 4ml.) or (100×12 mm., 8 ml.) are used for reactions which do not require boiling.

When a precipitate is to be separated by centrifuging a test-tube with a tapered bottom, known as *centrifuge tube* is usually employed. One should not boil a substance in these tubes.

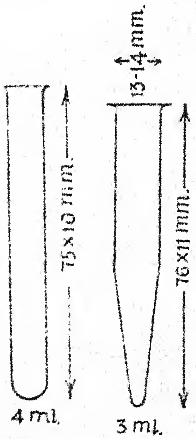


Fig. 1 (a) Test tube tubes (b) Centrifuge tubes

Stirrers. Whenever solutions do not mix in semimicro test-tubes or centrifuge tubes, the mixing is effected with the help of stirring rods. They are made by cutting 2 mm. diameter glass rod into 12 cm. lengths. One of the ends of the rod may be bent at 45° to

GROUP ANALYSIS

BASIC RADICALS

To the portion, soluble in water or dilute nitric acid, add dilute hydrochloric acid in excess, in cold and filter.

Residue
Silver Group : Pb, Hg and Ag. Boil the residue with water, and filter.

- *Filtrate* $PbCl_2$. Add acetic acid and K_2CrO_4. Yellow ppt. →*Pb*.
- *Residue* $AgCl+Hg_2Cl_2$. Add ammonia, and filter.
  - *Residue* Black →*Hg*(ous.)
  - *Filtrate* Add dil. HNO_3 in excess. White ppt.→*Ag*.

Filtrate :—Pass H_2S, till no further ppt. and filter.

Residue :—Sulphides of Hg, Pb, Cu, Cd, Bi, As, Sb and Sn. Shake with yellow ammonium sulphide, and filter.

- *Residue* :—Copper Group, Hg, Pb, Bi, Cu, Cd. Heat with HNO_3 (1 : 3), and filter.
  - *Residue* Hg and S. Dissolve in aqua regia, dilute, and (i) add $SnCl_2$→ greyish white ppt.→Hg. (ii) on Cu foil, →grey deposit →*Hg*.
  - *Filtrate* Pb, Bi, Cu, Cd. Add alcohol and dil. H_2SO_4, and filter.
    - *Residue* $PbSO_4$. Dissolve in amm. acetate and add K_2CrO_4. Yellow ppt. →*Pb*.
    - *Filtrate* Bi, Cu, Cd. Add NH_4OH in excess, and filter.
      - *Residue* $Bi(OH)_3$ Dissolve in dil. HCl and pour in excess of water. White ppt. →*Bi*.
      - *Filtrate* Cu, Cd. Add. conc. HCl and pass H_2S.
        - *Residue* Cu_2S. Dissolve in HNO_3 (hot) and add excess NH_4OH. Intense blue col.→*Cu*. Add acetic acid and K_4FeCy_6. Reddish brown ppt.→*Cu*.
        - *Filtrate* Dilute it and pass H_2S. Yellow ppt. →*Cd*.
- *Filtrate* : Arsenic Group. As, Sb and Sn. Add dil. HCl in excess. If white ppt. persists, rejt ; otherwise filter the ppt. and boil with conc. HCl and filter.
  - *Residue* As or S. Boil with conc. HNO_3, dilute, and add amm. molybdate and warm. Canary yellow ppt.→*As*.
  - *Filtrate* Sb, Sn. Divide in 2 pts.
    - Part I Add iron nails and heat, filter
      - *Residue* Black *Sb*. Dissolve in HNO_3+tartaric acid, dilute and pass H_2S. Orange ppt. →*Sb*.
      - *Filtrate* Add $HgCl_2$. White (grey) ppt.→ *Sn*.
    - Part II Test with Pt-Zn couple. Black deposit on Pt. →*Sb*.

Filtrate: Boil with HNO_3. Add excess of NH_4Cl and excess of NH_4OH. If interferring acids. *absent* filter

- *Residue* : Iron Group. Fe, Cr, Al hydroxides. Wash well. Add NaOH excess and Br water and boil. Filter.
  - *Residue* Fe. Dissolve in dil. HNO_3 and add K_4FeCy_6; Prussian blue colour →*Fe*.
  - *Filtrate* : Cr, Al. Divide in 2 portions.
    (1) To Part I, add acetic acid in excess, and lead acetate. Yellow ppt.→*Cr*.
    (2) To part II, add in excess dil. HNO_3, heat, and then add NH_4OH in excess. White ppt.→*Al*. (or boil part II with an excess of NH_4Cl. White ppt. →*Al*.)
- *If Phosphate present* Take the filtrate from Cu-As Group, boil off H_2S ; heat with HNO_3 and add NH_4Cl and NH_4OH. Add 5 ml. Na acetate and an excess of acetic acid, and filter.
  - *Residue* Test for Fe, Cr and Al as above.
  - *Filtrate* : Add $FeCl_3$ till light red or tea-colour. Boil and filter.
    - *Residue* Reject $FePO_4$.
    - *Filtrate* Add NH_4OH, warm, filter and with the filtrate proceed for Zn Group- etc.

Filtrate Pass H_2S, and filter.

- *Residue* : Zinc Group, Co, Ni, Zn, Mn. Shake with dil. HCl in cold, and filter.
  - *Residue*: Co and Ni. Dissolve in HCl (conc.) and $KClO_3$ and evaporate to dryness. Dissolve in water. Add $NaHCO_3$ in excess and Br water. Apple green col. in cold→*Co*. (confirm by borax bead—Blue) Heat. If blackens →*Ni*.
  - *Filtrate* Zn and Mn. Boil off H_2S and add excess of NaOH ; boil and filter.
    - *Residue* Mn Fuse with Na_2CO_3+ KNO_3 Green mass giving pink solution in water→*Mn*.
    - *Filtrate* Zn PassH_2S White ppt. →*Zn*.

Filtrate Concentrate and add ammonium carbonate in excess, and filter.

- *Residue* ; Calcium Group. Dissolve in acetic acid and add K_2CrO_4, and filter.
  - *Residue*: $BaCrO_4$ (Yellow) Flame test →green flame. .. *Ba*.
  - *Filtrate* Sr & Ca Add an excess of amm. sulphate, and filter.
    - *Residue* $SrSO_4$ (white) Flame test. →persistent crimson →*Sr*.
    - *Filtrate* add amm. oxalate. White ppt. *Ca*. Flame test.→ impersistent red. →*Ca*.
- *Filtrate* Add sodium phosphate. White crystalline ppt.→*Mg*.

Test for NH_4 radical by heating the original mixture. and NaOH. NH_3 smell→NH_4.

Test for Na and K in the original mixture by flame test. Na flame—Golden yellow K flame—violet when seen through two blue glasses.

serve as the handle. The sharp edges are firepolished by heating for a moment in a flame.

Suitable stirrers may also be constructed by drawing out glass rods (Fig. 2.)

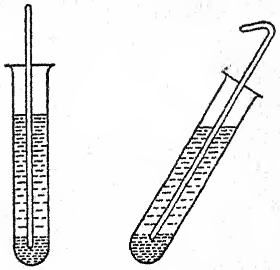


Fig. 2—Stirring rods

Droppers. Droppers are employed for handling liquids or solutions in semimicro analysis. Fountain pen ink droppers or eye-lotion droppers are familiar examples. (Fig. 3) A reagent bottle my be provided with a reagent dropper; its mouth may have a small spout which delivers spots as desired. A standard commercial form of medicine dropper with a tip of 1·5 mm. inside diameter and 3 mm. outside diameter delivers drops of dilute aqueous solutions about 0·05 ml. in volume (20 drops per 1 ml.). The droppers are fitted with rubber caps (or teats) to help in taking in the solutions and delivering them as desired.

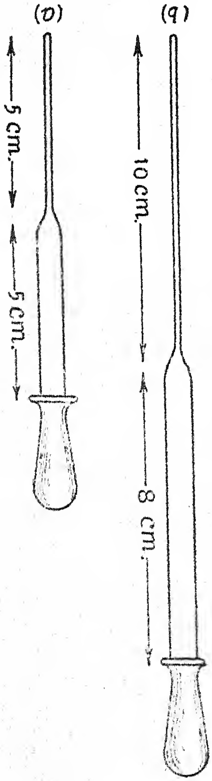


Fig. 3—Droppers

Reagent Bottles. A semimicro reagent bottle may be constructed by inserting a reagent dropper through a cork or rubber stopper that fits a 30 to 60 ml. bottle. One or two ounce dropping bottles may be purchased with stoppers usually of hard rubber or plastic composition. (Fig. 4) Concentrated inorganic acids attack these rubber or plastic teats. Glass dropping bottles may be used for these strong acids and corrosive reagents. Pipette bottles of 50 ml. capacity are also available. These bottles keep the reagents dust free.

Centrifuge. The separation of a precipitate from a supernatant liquid is carried out with the aid of a hand

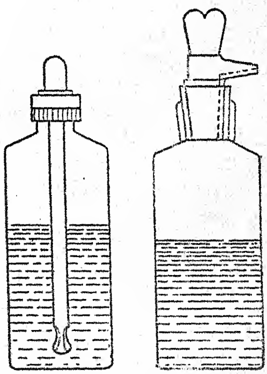


Fig. 4—Reagent bottles

centrifuge. (Fig.5) The separation is effected by the application of a centrifugal force, which may be several times that of gravity. The liquid containing the suspended precipitate is placed in a

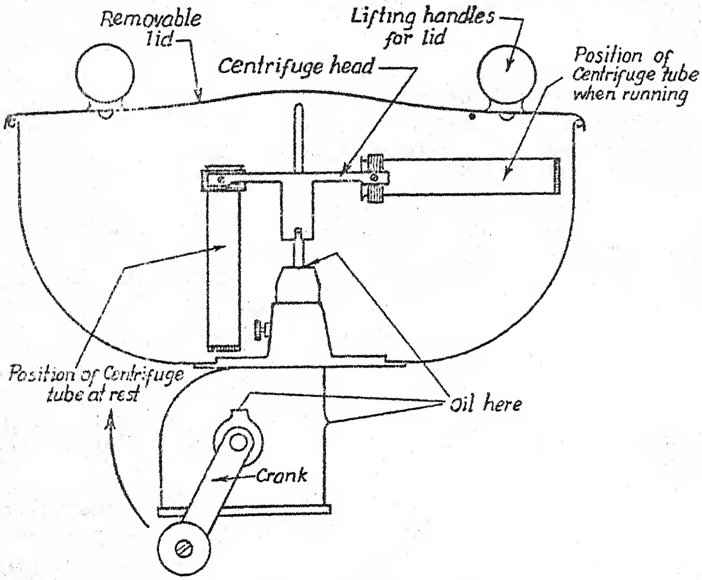


Fig. 5—Hand Centrifuge with cover

semimicro centrifuge tube. The tube and its contents and a similar tube containing an equal weight of water are placed in diagonally opposite buckets of the centrifuge, and the cover is placed in position; upon rotation for a short time, allowing the buckets to come to rest and removing the cover, it will be observed that the precipitate has settled down at the bottom of the centrifuge tube. (Some hand contrifuges are without the cover. They can be fixed at the projections of laboratory benches.) This operation is known as *centrifugation*; it saves the labour and time for filtration. One can now easily remove the supernatant liquid by means of a capillary dropper. The clear liquid is called *supernate* (or *centrifugate* or even *centrate*). The residue can be easily washed by taking it along with water and again centrifuging and discarding the supernatant liquid; the process may be repeated a number of times.

The following points may be borne in mind while using a hand-driven centrifuge:

(i) The two tubes should be of the same size and the same weight.

(ii) The tube should not be filled beyond 1 cm. from the top. Spilling would corrode the buckets.

(iii) Before centrifuging a precipitate contained in a centrifuge tube, prepare a balancing tube by adding sufficient distilled water from a dropper to an empty tube of the same capacity; the liquid levels in both tubes should be the same.

(iv) Introduce the tubes in diametrically opposite position in the centrifuge; the head (or *rotor* as it is called) will then be balanced. Fix now the cover in its place.

(v) Start the centrifuge slowly and smoothly, and bring to the maximum speed with a few turns of the handle. Maintain the maximum speed for 40 seconds, and then allow the centrifuge to come to rest of its own accord by releasing the handle.

(vi) Never use centrifuge tubes with broken or cracked lips.

Washing of Precipitates. Just as one washes the precipitate on the filter paper to remove the small amount of the solution present along with the precipitate, similarly the precipitates separated in the centrifuge tubes are also to be washed. They should be washed at least twice.

To wash a precipitate in the centrifuge tube, 5-10 drops of water or other wash liquid are added and the mixture is thoroughly stirred by stirring rod or platinum wire. The centrifuge tube is then counterbalanced against another similar tube containing water to the same level and centrifuged. The supernatant liquid is removed by a capillary dropper and the washing is again repeated.

Wash Bottles.—A 30 or 60 ml. wash bottle would serve the purpose. A plastic wash bottle is also available and is convenient. A small conical flask fitted with a hand blowing device and a small delivery would be good for hot water.

Removal and Addition of Drops. The drops of test solutions and agents are removed and carried by using glass tubing (20 cm. long and 3 mm. wide). The tubings may be slightly drawn at the tip to form a pipette (fig. 6). For *touching* a spot on a paper with reagent, a very small loop in a platinum wire may be utilised.

Spot plate. The mixing of drops of reacting solutions may be carried out either on the *spot plate*, in micro-porcelain crucibles (1 ml. capacity), or on filter paper. Spot plates are made from glazed porcelain, and usually contain 6-12 adjacent depressions (as in the painter's box for mixing colours) of equal size that hold about 0·5 to 1 ml. of the liquid. For colour reactions, white glazed plates are prescribed, and for white or lightly coloured precipitates, black spot plates or shallow black porcelain dishes may be used. An ordinary watch glass placed on a white or black paper would also work well.

Fig. 6

Warming device: For *warmig* the liquid in a micro-test-tube, a simple apparatus (fig. 7) constructed from the aluminium wire is useful. The micro-test-tubes are slipped through the openings and allowed to rest on their collars. The wire holder is fitted over a beaker, which can be filled with water at the desired temperature. There is a provision for two tubes for comparison.

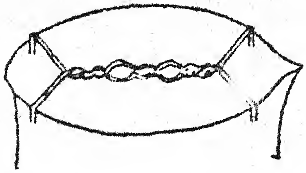


Fig 7

Micro-porcelain crucibles are used for *heating*, whenever necessary. They are usually heated on an asbestos mat, rather than over the direct flame. A silica watch glass is extremely useful for rapid *evaporations and ashing*.

Precipitations. Precipitations are carried out in centrifuge tubes, on spot plates or on drop reaction paper. In the first case, a drop of the precipitating agent is added to a drop of solution in a centrifuge tube. A sintered glass filter tube used for precipitation is shown in fig. 8. The precipitate is observed after centrifuging. In many precipitations, the small amounts of precipitates are readily made visible by shaking up the fine suspension with ether; the precipitate is more dense at the ether-water layer. The grains are visible on rotating the tube.

Fig. 8 Filter tube

Drop Reaction or Spot Test Paper. Whatman No. 120 is a soft variety of pure, highly porous paper and this can be used for reactions furnishing highly coloured precipitates. The precipitate does not spread very far in the paper because of the filtering action of the pores of the paper. The white paper serves as an excellent back-ground for dark or coloured precipitates. The "Spot paper, or Schleicher and Schull (No. 601)" my also be used. The ordinary filter paper placed in a Petri dish would also serve admirably.

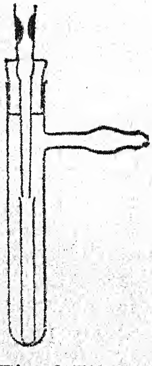


Fig. 9 Filtration device

Impregnated reagent paper can be made by laying the strips of quantitative filter paper in the reagent solution and drying in a drying oven. Or, the reagent may be sprayed over the filter paper by a sprayer.

Filtration Device—The *filtering* apparatus consists of an Emich filter stick fitted through a rubber stopper into a spout walled suction test-tube (fig. 9). The capillary of the filter stick touches inside the tip of micro-test-tube inside the filter tube. The spot test may then be carried out on the asbestos pad of the filter stick, and when the reaction is com-

plete on attaching the suction to a water pump, a drop of the clear filtrate comes through into the micro-test tube.

Caley's filter apparatus consists of a T-tube (fig. 10) of 6 mm. diameter, the short arm of which is closed by a rubber teat. The longest arm is closed by a piece of narrow vacuum tubing, and on the end is placed a small piece of filter paper cut to fit. A drop of the solution to be filtered is placed on the filter paper, while the capillary end is closed, and rubber teat is pressed. On releasing the teat, the drop filters into the T-tube, which can be easily transferred to the spot paper or on the spot plate.

For *heating*, a micro-flame of a micro-burner is utilised. *Microfusions* are done in loops of platinum wire.

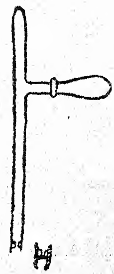


Fig. 10 Caley's Filter device

Cleaning of Apparatus. Scrupulous care for cleanliness should be taken. All apparatus should be thoroughly cleaned with a mixture of sodium dichromate (70 g.) in concentrated sulphuric acid (1 litre). One may also use a brush and cleansing powder. The apparatus is then rinsed several times with tap water and then with distilled water. The droppers and their rubber teats should also be washed with distilled water, and then allowed to dry on a linen glass cloth. At the end of the laboratory work, the clean apparatus is placed in a box with cover.

Section II—Organic Reagents for Spot Tests

Aluminon. $C_{19}H_{11}O_3(COONH_4)_3$, the ammonium salt of aurin tricarboxylic acid. 0·1% solution in water.—For Al.

Benzidine. $NH_2.C_6H_4.C_6H_4.NH_2$—Its 0·5% solution in 10% acetic acid.—For Pb.

a-Benzoin-oxime. $C_6H_5CHOH.C:(NOH).C_6H_5$. Dissolve 5 g. in 100 ml. of 95% alcohol.—For Cu.

Cacotheline (Nitrated-brucine). 0·25% aqueous solution.—For Sn.

Cinchonine-potassium iodide. Dissolve 1 g. of cinchonine in 100 ml. of water; add a few drops of conc. nitric acid and warm until solution takes place. After cooling add 2 g. of KI.—For Bi.

Cupferron. $C_6H_5N(NO)ONH_4$—2% aqueous solution.—For Fe.

1:8—*Dihydroxynaphthalene*—3:6—*disulphonic acid* (Chromotropic acid). Saturated aqueous solution—For Cr.

Dimethyl-amino-benzylidene-rhodanine. Dissolve 0·03 g. in 100 ml. of acetone.—For Ag.

Dimethylglyoxime. $C_4H_8N_2O_2$—Dissolve 1 g. in 100 ml. of 95% alcohol.—For Ni.

Dinitro-p-diphenylcarbazide. $CO(NH.NH.C_6H_4NO_2)_2$. 0·1%% solution in ethyl alcohol. For Cd.

Diphenylcarbazide- $(C_6H_5NH.NH)_2CO$.—(*a*) A cold saturated solution of the reagent is made in alcohol; saturate it with KCNS and a few crystals of KI.—For Hg.

(*b*) 0·2g. dissolved in 10 ml. of glacial acetic acid, diluted to 100 ml. with rectified spirit. For Mg.

Diphenylcarbazone.—$C_6H_5N{=}N—CO—NH.\ NH—C_6H_5$. 1% solution in ethyl alcohol.—For Hg (ic).

Diphenylthiocarbazone.—$C_6H_5—NH.NH—CS—N{=}N—C_6H_5$.—2-5 mg. in 100 ml. of carbon tetrachloride or chloroform.—For Pb.

Dipicrylamine (Hexanitrodiphenylamine).—$[C_6H_2(NO_2)_3]_2NH$. 2% solution in 0·1*N*—sodium carbonate (hot)—For K.

aa′—Dipyridyl. $(C_5H_4N)_2$. 0·01 g. of the substance dissolved in 0·5 ml. of alcohol. For Fe (ous).

Ethylene-diamine.—$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$.—For Hg (ic).

Ferron. (7-iodo-8-hydroxyquinoline-5-sulphonic acid). 0·2% aqueous solution. For Fe.

Gallocyanine. Its 1% aqueous solution. For Pb.

4-*Methyl*-1, 2-*dimercaptobenzene* (*Dithiol*).—$(SH)_2{\cdot}C_6H_3{\cdot}CH_3$—For Sn (ous).

p-*Nitrobenzene-azo-resorcinol* (*Magneson I*).—

$$O_2N\text{-}C_6H_4\text{-}N{:}N—C_6H_3(OH)_2.$$

Dissolve 0·001 g. of it in 100 ml. of 2 *N* NaOH.—For Mg.

p-*Nitrobenzene-azo-α-naphthol*, (*Magneson II*).—

$$O_2N—C_6H_4—N{:}N—C_{10}H_6(OH).$$

Dissolve 0·001 g. of the dyestuff in 100 ml. of *N*—NaOH.—For Mg.

4 *Nitronaphthalene-diazoamino-azobenzene* (*Cadion* 2B).—

$$O_2N.C_{10}H_6N{:}N—NH.C_6H_4{\cdot}N{:}N—C_6H_5.—$$

0·02% solution in alcohol.—For Cd.

α-Nitroso-β-naphthol.—$C_{10}H_6(OH)(NO)$. Make a saturated solution of the reagent in 50% acetic acid —For Co.

Orange IV.—Dissolve 0·01 g. of Tropeolin—OO in 130 ml. of water.—For Zn.

Oxine (8-Hydroxy-quinoline). C_9H_7NO. Dissolve 2 g. in 100 ml. of 2 *N* acetic acid.—For Mg.

o-*Phenanthroline.* $C_{12}H_8N_2$. 0·1% aqueous solution.—For Fe.

Picrolonic acid.—1-p-Nitrophenyl-3-methyl-4-nitro-5-pyrazolone).—For Ca.

Pyrogallol. 1:3:5.$C_6H_3(OH)_3$—0·5g. in 5 ml. of water—For Bi.

Quinaldinic acid (Quinoline-α-carboxylic acid). $C_9H_6N.COOH$, 1 g. of the acid is neutralised with NaOH and diluted to 100 ml.—For Zn.

Quinalizarin. (1:2:5:8 Tetrahydroxyanthraquinone). 0·50% solution in 0·1 *N* NaOH.—For Al and Mg.

Rhodamine B.—Dissolve the dyestuff 0·01 g. in 100 ml. of water.—For Sb.

Rubeanic acid.—$NH_2.CS.CS.NH_2$.—0·5% solution in 95% ethyl alcohol.—For Cu.

Sodium dihydroxytartrate-osazone.—

$$(C_6H_5.NH—N:C—COONa)_2$$—For Ca.

Salicylaldoxime. $HON:CH.C_6H_4.OH$. Dissolve 1 g. in 5 ml. of cold ethyl alcohol.—For Cu.

Sodium rhodizonate. $(CO.CO.C.ONa)_2$. 0·5% solution in water—For Ba and Sr.

Sulphosalicylic acid. $SO_3H.C_6H_3(OH)COOH$.—Dissolve 5 g. in 100 ml. of water.—For Fe.

Tetra Base (*Tetramethyl-diamino-diphenylmethane.*—

$$CH_2[C_6H_4N(CH_3)_2]_2.—$$

Dissolve 5 g. in 100 ml. of water; or 0·5 g. of the base in a mixture of 20 ml. of glacial acetic acid and 80 ml. of 96% ethyl alcohol.

Thiosinamine. $NH_2.CS.NH(CH_2.CH.CH_2)$.—Dissolve 5 g. of the reagent in 100 ml. of water.—For Cd.

Thiourea. $NH_2.CS.NH_2$.—Prepare its 10% solution in water.—For Bi.

Titan yellow. (Clayton yellow)—Prepare its 0·1% solution in water.—For Mg.

Section III—Use of Organic Reagents in Qualitative Analysis.

LEAD

1. *"Tetra Base" or tetramethyldiamino-diphenyl methane.*

Place 1 ml. of the test solution in 5 ml. centrifuge tube, add 1 ml. of KOH (2*N*) and 1 ml. of 3% hydrogen peroxide. Separate the precipitate of lead plumbate; add 2 ml. of the reagent, shake and centrifuge. Supernatant liquid would be coloured blue.

The ions of Bi, Mn, Co and Ni (also Ce and Tl) give a similar reaction.

Prepare the reagent by dissolving 0·5 g. of the base in a mixture of 20 ml. of glacial acetic acid and 80 ml. of 96% ethyl alcohol.

2. *Benzidine Reagent* (*benzidine blue*):

Place a drop of the test solution upon the drop-reaction paper, and treat successively with 2 drops of 3*N* NaOH and 1 drop of saturated bromine water. Add 2 drops of 1:1 ammonia solution, remove the excess of ammonia by waving the paper on a small flame. Add two drops of the reagent: a blue colour is developed.

The ions of Bi, Mn, Co, Ni, Ag (and also Ce and Tl) answer this test, but if performed in an alkaline extract, only Tl interferes.

3. *Gallocyanine Reagent*:

Place a drop of the test solution upon drop-reaction paper, followed by a drop each of 1% aqueous pyridine and gallocyanine reagent (*blue*). Remove the excess of the reagent by placing several filter papers beneath the drop reaction-paper and adding drops of the pyridine solution to the spot until the wash liquid percolating through is colourless; move the filter papers to a fresh position after each addition of pyridine. A deep violet spot is produced.

The test is applicable to finely divided *lead sulphate*. Therefore, if Ag, Bi, Cd or Cu is present, transfer a drop of the test solution to a drop reaction-paper, and add a drop of 2*N* sulphuric acid to fix Pb as $PbSO_4$; remove the soluble sulphates of Ag, Cu etc. by washing with 2*N*-sulphuric acid, then with spirit; dry the paper on water bath and then apply the gallocyanine test.

The reagent consists of a 1% solution of gallocyanine in water.

4. *Diphenylthiccarbazone Reagent* (*Dithizone Reagent*):

Place 1 ml. of the neutral or faintly alkaline solution in a micro test-tube, introduce a few small crystals of KCN and then

2 drops of the reagent; shake for 30 sec. The green colour of the reagent would change to red.

Heavy metals like Ag, Hg, Cu, Cd, Sb, Ni, Zn etc. interfere with this test if not carried in presence of an excess of KCN; an excess of KOH is also necessary if Zn is present.

The reagent is prepared by dissolving 2-5 mg. of dithizone in 100 ml. of carbon tetrachloride or chloroform.

SILVER

Para-dimethylamino-benzylidene-rhodanine Reagent:

Spot the test solution on drop-reaction paper, add 1 drop of N-nitric acid and then a drop of the reagent. A red-violet precipitate or stain is formed.

If Hg is also present, treat a drop of the test solution with a drop of 5% KCN solution, and then with the reagent, and a drop of $2N$ nitric acid. A red colour would be obtained if Ag is present.

The reagent consists of a 0·03% solution of the substance in acetone or in alcohol.

MERCURY (IC)

1. *Ethylenediamine Reagent*:

A dark blue-violet precipitate of the complex $[Cu\ en_2][HgI_4]$ is formed when a mercuric salt in neutral or faintly ammoniacal solution is treated with excess of 2% KI solution, followed by the ethylenediamine reagent.

The reagent is prepared by treating a solution of cupric sulphate with an aqueous solution of ethylenediamine (5-6 times the theoretical quantity), until the dark blue-violet coloration, due to the $[Cu\ en_2]^{++}$ ion appears and does not intensify in colour on further addition of the base.

Cadmium ions interfere in this reaction.

2. *Diphenylcarbazone Reagent*:

Place a drop of the test solution and a drop of $0·2N$ nitric acid upon drop reaction paper, which has been moistened with the reagent. A violet or blue coloration would result.

The reagent consists of a 1% solution of the substance in 90-100% ethyl alcohol.

BISMUTH

1. *Pyrogallol Reagent*:

0·5 g. of pyrogallol is dissolved in 5 ml. of water. This is added to a hot solution of a bismuth salt faintly acid with dilute

HCl or nitric acid. It would furnish a yellow precipitate of the complex Bi ($C_6H_6O_3$). Antimony interferes with this test and therefore it should be absent before trying this test.

2. *Cinchonine-KI Reagent*:

This reagent forms orange-red coloration or precipitate with a Bi salt; the precipitate has the composition of bismuth-cinchonine-iodide (BiI_3-cinchonine, HI) in faintly acid solution.

Moisten a piece of drop reaction paper with the reagent and place a drop of the slightly acid test solution upon it. An orange-red spot is obtained.

Pb, Hg and Cu salts interfere with this test.

The reagent is prepared by dissolving 1 g. of cinchonine in 100 ml. of hot water, containing a few drops of nitric acid; the solution is cooled and then 2 g. of KI is added.

3. *Thiourea*:

It furnishes intense yellow coloration in presence of dilute nitric acid (test on spot plate or drop reaction paper). Hg (ous), Ag, Sb, Fe (ic) and chromates interfere, and therefore they should be absent.

The reagent is 10% aqueous solution of thiourea.

COPPER

1. a—*Benzoin Oxime Reagent* (*Cupron Reagent*):

It furnishes a green precipitate of copper benzoin oxime, Cu ($C_{14}H_{11}O_2N$), insoluble in dilute ammonia. Addition of sodium potassium tartrate would prevent the precipitation of such other metallic salts as may interfere. The reagent is specific for Cu in ammoniacal tartrate solution.

Treat drop-reaction paper with a drop of weakly acid test solution and a drop of the reagent, and then hold it over ammonia vapour. A green coloration would be obtained.

Prepare the reagent by dissolving 5 g. of α-benzoin oxime in 100 ml. of 95% alcohol.

2. *Salicylaldoxime Reagent*

Place a drop of the test solution (which has been first neutralised and then acidified with acetic acid) in a micro test-tube and add a drop of the reagent. A yellow-green precipitate or opalescence is obtained.

The reagent is prepared by dissolving 1 g. of the substance in 5 ml. of cold alcohol and pouring the solution drop by drop into 95 ml. of water, the mixture shaken and filtered.

3. *Rubeanic acid Reagent* (*Dithio-oxamide Reagent*)

Place a drop of the neutral test solution upon drop-reaction paper, expose it to ammonia vapour and a drop of the reagent. A black or greenish-black spot is produced.

If *nickel* is present : Impregnate drop-reaction paper with the reagent and add a drop of the test solution acidified with acetic acid. Two zones are formed: the central olive green or black ring is due to copper, and the outer blue-violet ring is due to nickel.

If *cobalt* is present : The central green or black ring of copper is surrounded by a yellow-brown ring of cobalt.

The reagent consists of a 0. 5% solution of rubeanic acid in 95% ethyl alcohol. It should be freshly prepared.

CADMIUM

1. *Dinitro-p-diphenylcarbazide Reagent*

Place a drop of the acid, neutral or ammoniacal test solution on a spot plate and mix it with 1 drop of 10% NaOH solution and 1 drop of 10% KCN solution. Introduce 1 drop of the reagent and 2 drops of 40% formaldehyde solution. A brown precipitate is formed which rapidly changes to greenish-blue (compare with a blank solution).

The reagent consists of a 0·1% solution of the substance in alcohol.

2. *4-nitronaphthalene-diazoamino-azobenzene Reagent* (*Cadion 2B Reagent*) :

Place a drop of the reagent on drop reaction paper, add 1 drop of the test solution (slightly acidified with acetic acid containing a little K-Na-tartrate), and then 1 drop of 2*N* KOH. A bright pink spot, surrounded by a blue circle is produced. (Na-K-tartrate prevents the interference of Cu, Ni, Co, Fe, Cr and Mg; Ag and and Hg also interfere which should be removed).

The reagent is prepared by dissolving 0·02 g. of the substance in 100 ml. of ethyl alcohol, adding 1 ml. of 2*N* KOH. (Do not warm the solution.)

ANTIMONY

Rhodamine-B Reagent (*Tetraethyl-Rhodamine Reagent*)

The test solution should be strongly acidic with HCl, and the antimonious antimony oxidised by the addition of a little solid sodium or potassium nitrite. Place 1 ml. of the reagent

on a spot plate and add 1 drop of the test solution. The bright red colour of the reagent changes to blue.

The reagent is prepared by dissolving 0·01 g. of rhodamine-B in 100 ml. of water (or 0.05 g. of the reagent in a 15% solution of KCl in $2N$ HCl).

STANNOUS

1. *Dimethylglyoxime-Ferric chloride Test*:

No coloration is obtained when ferric salts are mixed with the dimethyl glyoxime reagent and a little ammonia solution, but if a trace of ferrous salt is present (produced by reduction with stannous ions), a deep red coloration due to the formation of ferrous dimethylglyoxime chelate complex is obtained.

Place 0·2 ml. of the test solution containing stannous tin in a micro test-tube, acidify (if necessary) with dil. HCl, add 0.2 ml. of $0 \cdot 1N$ $FeCl_3$ solution, followed by 0·3 ml. of 5% tartaric acid solution (to prevent the formation of ferric hydroxide), 3 drops of dimethylglyoxime reagent and about 0·5 ml. of $4N$ ammonia solution. A red coloration is obtained.

The reagent solution is obtained by dissolving 1 g. dimethylglyoxime in 100 ml. of ethyl alcohol.

2. *Cacotheline Reagent* (a nitro-derivative of brucine alkaloid).

The test solution should be acidic ($2N$ HCl). Tin if stannic should be reduced by treatment with aluminium or magnesium filings and HCl and the solution filtered.

Impregnate drop reaction paper with the reagent, and before the paper is quite dry, add a drop of the test solution. A violet spot, surrounded by a less coloured zone, appears on the yellow paper (one may also test in a micro-test-tube).

The reaction is sensitive but not selective. The interfering ions are Hg, Bi, Sb, Co, Ni (V, U, Te, Au, Pd, Se, Mo, and W).

The reagent is 0.25% solution of cacotheline in water.

3. *Diazine Green Reagent* (a dyestuff obtained by coupling diazotised safranine with dimethylaniline):

Mix one drop of the test solution on a spot plate with 1 ml. of the reagent. The colour changes from blue to violet or red (compare with a blank).

The reagent is prepared by dissolving 0·01 g. of the dyestuff in 100 ml. of water.

Titanous salts also give this test, but not ferrous. The solution of the sulphides in HCl is reduced with iron wire, Al or Mg powder and a drop of this reduced solution is used for Sn (II) test.

4. 4-*Methyl*-1 : 2—*dimercapto-benzene Reagent* (*Dithiol Reagent*):

Place two drops of the test solution, acidify with dil. HCl in a micro-crucible and add 3 drops of the reagent and warm; a red colour or precipitate develops.

The interfering ions are Ag,Pb,Hg,Cd,As,Sb (yellow precipitate); Bi (red precipitate); Cu,Ni,Co (black).

The reagent is prepared by dissolving 0·2 g. of the substance in 100 ml. of 1% NaOH solution and adding 0·3 g. of thioglycollic acid.

IRON (OUS)

1. *aa′—Dipyridyl reagent* :

Test on a spot plate a drop of the faintly acidified test solution with 1 drop of the reagent. A red coloration is obtained. (Or test with drop reaction paper, impregnated with the reagent, and dried, with a drop of the test solution: red or pink spot).

The reagent is prepared by dissolving 0·01g. of the substance in 0·5 ml. of alcohol or in 0·5 ml. of 0·1 *N* HCl.

2. *Dimethylglyoxime Reagent*:

Mix a drop of the test solution with a small crystal of tartaric acid; introduce a drop of the reagent, followed by 2 drops of ammonia solution. A red coloration appears. The coloration fades on standing due to the oxidation of ferrous to ferric.

The reagent consists of a 0·1% solution of the substance in alcohol.

Ni,Co and Cu salts interfere in this test.

3.0—*Phenanthroline Reagent*:

Place a drop of faintly acid test solution on a spot plate and add 1 drop of the reagent. A red colour is obtained.

If iron is present in the *ic* form (FeIII), it must first be reduced to *ous* (Fe II) form with hydroxylamine hydrochloride.

The reagent is a 0·1% solution of the substance in water.

IRON (*IC*)

1. *Cupferron Reagent* [Ammonium salt of nitrosophenylhydroxylamine, [$C_6H_5N(NO)ONH_4$]:

The reagent furnishes reddish-brown precipitate with ferric salts in presence of hydrochloric acid. Al and Cr are not precipitated under these conditions, i. e., if the solution is strongly acidic.

The reagent is prepared by dissolving 2 g. of the solid in 100 ml. of water. It should be freshly prepared or stocked in presence of a piece of ammonium carbonate.

2. *7-Iodo-8-hydroxyquinoline-5-sulphonic acid* (*Ferron Reagent*).

Place a few drops of the slightly acid test solution in a micro test-tube and add a drop of the reagent. A green coloration appears.

The reagent solution is prepared by dissolving 0·2 g. of the substance in 100 ml. of water.

ALUMINIUM

1. *Aluminon Reagent* (ammonium salt of aurin tricarboxylic acid):

The test is applied to the aluminium hydroxide precipitate; in 2 ml. of *M* HCl, this precipitate obtained from the group analysis is dissolved, and 2 ml. of 3*M* ammonium acetate solution is added, and then 2 ml. of 0·1% aqueous solution of the reagent. The mixture is shaken and allowed to stand for 5 minutes, and then is added an excess of ammoniacal ammonium carbonate solution to decolorise the excess of the dyestuff and lakes due to the traces of Cr and silica. Aluminium gives a bright red precipitate (or colour) which persists in the alkaline solution.

The reagent is prepared by dissolving 0·1 g. of the substance in 100 ml. of water.

2. *Alizarin Reagent* :

Soak the filter paper or drop-reaction paper in a saturated alcoholic solution of alizarine and dry it. Place a drop of the acid test solution on the paper and hold it over ammonia vapours until a violet colour (due to ammonium alizarinate) appears. In the presence of large amounts of aluminium, the colour is visible almost immediately; aluminium gives a red lake with the alizarine reagent. (It is best to dry the paper at 100° when the violet colour due to ammonium alizarinate disappears owing to its conversion into ammonia and alizarine).

The reagent is a saturated alizarine solution in alcohol.

3. *Alizarin-S* (*or sodium alizarin sulphonate*) *Reagent* :

Place a drop of the test solution (aluminium hydroxide precipitate just dissolved in sodium hydroxide) on the spot plate; add a drop of the reagent, then drops of acetic acid until the violet colour just disappears, and 1 drop in excess. Red precipitate or colour would appear if aluminium is present.

The reagent is a 0·1% solution of the substance in water.

4. *Quinalizarin Reagent* (1:2:5:8—Tetrahydroxy-anthraquinone):

Place a drop of the test solution upon the reagent paper; hold it for a short time over a bottle containing strong ammonia and then over glacial acetic acid until the blue colour of ammonium quinalizarinate first formed disappears, and the unmoistened paper regains the brown colour of free quinalizarin. A red-violet or red spot is formed.

The reagent paper is prepared by soaking quantitative filter paper in a quinalizarine solution (0·01g. dissolved in 2 ml. of pyridine and then diluting with 20 ml. of acetone.).

CHROMIUM

Convert chromium salt to a chromate by oxidising with bromine water in an alkaline solution, or by treating with an alkali persulphate (in the presence of a trace of silver salt, which acts as a catalyst).

1. *Diphenylcarbazide Reagent* :

Place a drop of the test solution in mineral acid on a spot plate; introduce a drop of saturated bromine water, then add 2-3 drops of 2*N*-KOH (render the solution alkaline to litmus). Mix thoroughly, add a crystal of phenol, then a drop of the reagent, and finally 2*N* sulphuric acid drop by drop until the red colour (from the reaction between the reagent and the alhali) disappears. A blue-violet coloration is obtained.

The reagent is 1% solution of the substance in alcohol.

2. 1:8-*Dihydroxynaphthalene*-3: 6-*disulphonic acid Reagent* (*Chromotropic Reagent*):

Place a drop of the test solution in semi-micro test-tube, add a drop of the reagent, a drop of dilute nitric acid (1:1) and dilute to 2 ml. Chromates give red coloration.

The reagent is a saturated solution of the substance in water.

COBALT

1. *α-Nitroso-β-naphthol Reagent*:

The reagent furnishes reddish-brown precipitate of cobalti-nitroso-β-naphthol (inner complex) in acidic solution (HCl or

acetic acid). The precipitate is extracted with CCl_4 (claret-coloured solution).

The precipitates are also given by Fe (II and III) Ni and uranyl salts. Ni complex is soluble in dil. HCl; Fe(III) does not furnish precipitate in presence of sodium fluoride and uranyl ion may be removed as uranyl phosphate.

Place a drop of the faintly acid solution to be tested on the drop reaction paper, and add a drop of the reagent. A brown stain is produced if cobalt is present.

The reagent is a 1% solution of the substance in 50% acetic acid (or in alcohol or acetone).

2. *Sodium 1-Nitroso-2-hydroxynaphthalene-3 : 6-di-sulphonate* Reagent (Nitroso-R-salt Reagent).

Place a drop of the neutral test solution (buffered with sodium acetate) on a spot plate, and add 2-3 drops of the reagent. A red colouration is obtained.

The reagent is 1% solution of the substance in water.

3. *Rubeanic acid Reagent (Dithio-oxamide Reagent)*:

Place a drop of the test solution upon drop-reaction paper, hold it in ammonia vapour, and then add a drop of the reagent. A brown spot or ring is obtained.

The reagent is a 1% solution of the substance in alcohol.

NICKEL

1. *Dimethyl glyoxime Reagent* ($C_4H_8O_2N_2$):

Place a drop of the test solution on the drop-reaction paper, add a drop of the reagent, and hold the paper over ammonia vapours. A red spot is obtained.

The reagent is 1% solution of the substance in rectified spirit. The reagent may also be used for quantitative precipitation of nickel.

The interfering ions are: Fe (II), Co (if present in large excess), Pd, Pt and Au.

2. *α-Nitroso-β-naphthol Reagent*:

Nickel salts furnish brown precipitate with the reagent, which is soluble in dil. HCl (difference from Co which gives a reddish-brown precipitate, insoluble in dil. HCl).

3. *Rubeanic Acid Reagent*:

Place a drop of the test solution upon drop-reaction paper, hold it over ammonia vapour and add a drop of the reagent. A blue or blue-violet spot is obtained.

The reagent is 1% solution in alcohol.

MANGANESE

Formaldoxime Reagent (HCH:NOH)

Place 2 ml. of the test solution (just alkaline with 4*N*-NaOH) into a semimicro test-tube, and add 1 drop of the reagent. A red coloration is obtained.

The reagent is a 2·5% solution in water.

ZINC

1. *Quinaldinic Acid Reagent* (Quinoline-α-carboxylic acid);

A fer drops of this reagent when added to a solution containing Zn ions (faintly acid with acetic acid) furnish a white precipitate of the zinc complex, soluble in ammonia and in mineral acids. The ions interfering are of Cu, Cd, Fe, Cr, (also uranyl); Co, Ni and Mn ions have no effect. The test is very sensitive for Zn.

The reagent is obtained by neutralising 1 g. of the substance with NaOH solution and dilution and diluting to 100 ml.

2. *Potassium ferricyanide-p-Phenetidine Test.*—

Prepare the reagent by mixing 6 drops of 2% potassium ferricyanide solution, 2 drops of *N*-sulphuric acid, and 6 drops of 2% p-phenetidine hydrochloride solution.

To 0·1 ml. of the freshly prepared reagent on a spot plate, add a drop of the test solution. A purple to blue coloration or precipitate would appear if Zn is present.

BARIUM

Sodium Rhodizonate Reagent:

Place a drop of the neutral or faintly acid test solution upon drop-reaction paper and a drop of the reagent. A brown or reddish-brown spot is obtained.

Ca and Mg salts do not interefere in this test; Sr salts furnish a precipitate which is completely soluble in dil. HCl. If Sr is present, then the reddish-brown stain of barium rhodizonate is treated with dil. HCl (0.5*N*), the Sr stain would dissolve, while the barium stain would be converted to brilliant red acid salt. (Carry out the reaction on drop-reaction paper)·

The reagent is 0·5% aqueous solution of sodium rhodizonate (freshly prepared).

STRONTIUM

Sodium Rhodizonate Reagent:

If Ba is *absent*, place a drop of the neutral test solution on drop-reaction paper or on a spot plate; add a drop of the reagent. A brownish-red coloration or precipitate would be obtained.

If Ba is *present*: Impregnate quantitative filter paper with a saturated solution of potassium chromate and dry it. Place a drop of the test solution on this paper and after a minute, place 1 drop of the reagent on the moistened spot. A brownish-red spot or ring is formed.

CALCIUM

1. *Sodium dihydroxytartrate Osazone Reagent*:

Place a drop of the neutral test solution on a black spot plate (or on a black watch glass). Add a tiny fragment of the solid reagent. If calcium is absent, the reagent dissolves completely. The presence of calcium is indicated by the formation over the surface of the liquid of a white film which finally appears as a dense precipitate.

2. *Picrolonic Acid* (1-p-Nitrophenyl-3-methyl-4-nitro-5-pyrazolone) *Reagent*:

Place a drop of the test solution (neutral or acidified with acetic acid) in the depression of a *warm* spot plate and add 1 drop of a saturated aqueous solution of picrolonic acid. Characteristic rectangular crystals are produced.

MAGNESIUM

1. *Diphenyl-carbazide Reagent* (C_6H_5.NH. NH.CO.NH.NH.-C_6H_5):

Treat the magnesium salt solution with NaOH solution, and get a precipitate of $Mg(OH)_2$; then treat with a few drops of the reagent and filter. Wash the precipitate with hot water. A violet-red colour would indicate the presence of Mg(an adsorption complex is formed).

The reagent is obtained by dissolving 0·2g. of the substance in 10 ml. of giacial acctic acid and diluting to 100 ml. with rectified spirit.

2. 8-*Hydroxy-quinoline Reagent* (*Oxine Reagent*):

Treat the solution containing Mg salt and a little ammonium chloride with 1-2 ml. of the reagent in (which has been made alkaline by adding ammonia solution in excess : 3-4 ml. of ammonia solution), and heat the mixture to boiling. A yellow precipitate of the complex is obtained.

The reagent is a 2% solution of oxine in 2*N* acetic acid.

3. p-*Nitrobenzene-azo-resorcinol Reagent* (*Magueeon I Reagent*):

The reagent is a dyestuff which is adsorbed upon magnesium hydroxide in alkaline solution, furnishing a blue lake.

Take 2 ml. of the test solution (acidified with HCl), and treat with 1 drop of the reagent and sufficient *N* NaOH solution (2-3 ml.). A blue precipitate would appear if Mg is present. (In semimicro test, perform a blank test side by side). All metals except the alkali metals must be absent while performing this test.

The reagent (for macro analysis) is a 0.5% solution of the substance in 0·25 *N* NaOH solution.

Spot Test: Place a drop of the test solution on a spot plate, and add 1-2 drops of the reagent. Add a drop of *N*-NaOH. A blue precipitate or a blue colour would be obtained (depending on the Mg concentration). Perform a blank test with distilled water. Filter paper or drop-reaction paper should not be used.

The reagent is 0·001 g. of the dyestuff dissolved in 100 ml. of *N*-NaOH.

4. *p-Nitrobenzene-azo-α-naphthol* (*Magneson II*)

It furnishes the same colour changes as Magneson I, but is more sensitive (1 in 250,000).

5. *Titan Yellow Reagent* :

It is a water-soluble dye-stuff, yellow in colour. It is adsorbed by $Mg(OH)_2$ producing a deep red colour or precipitate. (Ba and Ca do not react but intensify the red colour). Elements of Groups I to IIIB should be removed (Ag group to Zinc group).

Place a drop of the test solution on a spot plate, add a drop of the reagent and a drop of 0·1 *N* NaOH. A red colour or red precipitate is produced.

The reagent is 0·1% aqueous solution of the dyestuff.

6. *Quinalizarin Reagent* :

Place a drop of the test solution and a drop of distilled water in adjacent cavities of a spot plate and add two drops of the reagent to each. If the solution is acid, it will be coloured yellowish-red by the reagent. Add 2*N* NaOH until the colour changes to violet and a further excess to increase the volume by 25-50%. A blue precipitate or coloration appears. The blank one has a blue-violet eolour.

The reagent is 0·01-0·02g. of the substance in 100 ml. of alcohol.

POTASSIUM

Dipicrylamine Reagent (*Hexanitro-diphenylamine Reagent*)

Place a drop of the neutral test solution upon drop reaction paper and immediately add a drop of slightly alkaline reagent.

An orange-red spot is obtained (which remains unaffected when treated with 1-2 drops of 2*N* HCl).

The reagent is prepared by dissolving 0·2g. of the substance in 20 ml. of boiling 0·1 *N*-sodium carbonate, and filtering the cooled liquid.

SODIUM

Spot tests may be done by (i) *uranyl magnesium acetate* solution which furnishes yellow crystalline precipitate with concentrated sodium solutions. (The reagent is prepared by mixing 10 g. uranyl acetate dissolved in 6 g. of glacial acetic acid and 100 ml. of water.—Solution A; 33 g. of magnesium acetate are dissolved in 10 g. of acetic acid and 100 ml. of water.—Solution B. The two solutions A and B are mixed and allowed to stand for 24 hours and filtered.)

(*ii*) *Uranyl zinc acetate* is sometimes preferred to uranyl magnesium acetate. It also furnishes yellow crystalline precipitate with sodium ions. The reaction is fairly selective. The reagent is prepared in the same way as indicated above: Solution A—10 g. uranyl acetate, 6 g. acetic acid (30%) and water to make 50 ml. Solution B—30 g. zinc acetate, 3g. of 30% acetic acid, and water to 50 ml.

AMMONIA

It is best tested with *Nessler's Reagent*: 10 g. of KI in 10 ml. of water, saturated mercuric chloride solution (60 g. per litre) then added till a permanent precipitate is formed, then 80 ml. of 9*M*-KOH solution added and diluted to 200 ml. The reagent furnishes brown precipitate or brown or yellow coloration with ammonium salts.

Mix a drop of the test solution with a drop of conc. NaOH solution on a watch glass. Transfer a micro drop of the resulting solution or suspension to drop reaction paper and add a drop of Nessler's reagent. A yellow or orange red stain or ring is produced.

(*ii*) *Sodium cobaltinitrite* solution furnishes yellew precipitate of ammonium cobaltinitrite with ammonium ions.

(*iii*) *Chloroplatinic acid* solution furnishes yellow crystalline precipitate with ammonium ions. This decomposes when warmed with NaOH solution evolving ammonia.

(*iv*) Saturated *sodium hydrogen tartrate* solution furnishes white precipitate with ammonium salts (this is slightly more soluble than the corresponding K-salt; it evolves ammonia when heated with NaOH solution.)

(*v*) *p-Nitrobenzene-diazonium chloride Reagent* (*Riegler's Reagent*)

Place a drop of neutral or slightly acid test solution on a spot plate, followed by a drop of the reagent and a fine granule of CaO between the two drops. A red zone forms round the calcium oxide (carry out a blank test).

The reagent may be prepared by diazotising p-nitraniline with sodium nitrite and hydrochloric acid.

Section IV—Group Analysis—Basic Radicals

In order to analyse the mixture qualitatively by the semimicro method, take a small quantity of the mixture (covering one spatula) and prepare its solution in a 10 ml. test-tube.

The insoluble chlorides of Group I must be precipitated from an acid solution. If the unknown solution is basic or ammoniacal, it should be acidified first with nitric acid. Remember that in an ammoniacal solution, silver is present as $[Ag(NH_3)_2]^+$ ion, and in sodium hydroxide solution, lead is in the form of $HPbO_2^-$ ion. Upon acidification with dilute nitric acid in excess, these ions are converted into simple cations.

Group I-Ag, Hg (ous) and Pb.

The mixture dissolved in an excess of dil. HNO_3 is cooled and 1-2 ml. of it taken. Add to it drop by drop 4 *N* HCl with stirring. After adding 5-10 drops of the acid, centrifuge, add an additional 4-5 drops of 4*N* acid to the clear supernate. If a precipitate forms, add an additional 5-10 drops of 4*N* HCl. Centrifuge, then add 4-5 drops more of HCl. to ensure complete precipitation. Stir thoroughly and centrifuge.

Analyse the precipitate (or residue) for AgCl, Hg_2Cl_2 and $PbCl_2$.

Use the supernate for the subsequent groups.

Residue, AgCl, $PbCl_2$ and Hg_2Cl_2. Wash the precipitate with 1-2 ml. of water. Then add 4 ml. of distilled water. Heat to boiling and centrifuge immediately. Decant the supernate to a clean test-tube. Again add 3 ml. of water to the residue, heat to boiling and centrifuge immediately.

Add the supernate to the previous supernate.

<table>
<tr>
<td rowspan="2">Supernate Solution→ Pb—Divide in 2 portions.
(i) Add about 5 drops of 6M-acetic acid and 2 ml. of 0.5M K_2CrO_4→ Yellow ppt.—Pb.

(ii) Add one drop: of KI solution Yellow cryst. silky needles of PbI_2—Pb.</td>
<td colspan="2">Residue→AgCl, Hg_2Cl_2
Wash the ppt. with hot distilled water. Now add 4 ml. of warm 6 N-ammonia solution. Centrifuge. Decant the supernate to a clean tube.</td>
</tr>
<tr>
<td>Supernate— $[Ag(NH_3)_2]^+$
1. Add 6M-nitric acid (5-6 ml.)→ white ppt. of Ag Cl→Ag.
2. Test another portion with KI→Yellow ppt. of AgI →Ag.</td>
<td>Residue : $HgNH_2Cl+Hg°$.
If black—Hg.
Dissolve the black ppt. in HCl (conc.) (4 drops) and bromine water (3 drops) ; heat : boil off excess of HCl, add 1 ml. of water and test with $SnCl_2$—white or grey ppt.—Hg.</td>
</tr>
</table>

Group II

Use the supernate obtained from Group I. To the supernate solution, add 1 ml. of 4 N-H_2SO_4 and 1 ml. of alcohol and centrifuge. Separate the supernate and the residue. Add again 1 ml. of 4N-H_2SO_4 and 1 ml. of alcohol to the supernate, and centrifuge. Collect all the residue at one end and the supernate at the other :

Precipitate or residue
Sulphates of Ba, Sr, Ca

Supernate solution
Add 5 drops of dil. H_2SO_4 and again centrifuge to ensure complete separation of Ba group. Transfer the solution to a beaker and boil to half the volume; cool and add saturated Br-water drop by drop till the solution is yellow, *i. e.*, till Br is in excess. Boil off the excess of Br. Add 4*N*-ammonia till just alkaline (test with litmus paper) and then add *N*-HCl till just acidic, add 3 drops more of HCl, heat to boiling and pass H_2S slowly, and centrifuge.

Precipitate or residue
Cu Group—Hg, Cu, Bi, Cd.
As Group—As, Sb, Sn.

Supernate solution
Evaporate the solution to dryness. To the residue, add 1 ml. of conc. HCl, heat to boiling and pass H_2S; and centrifuge. If any ppt.→As^{+5} (from arsenate). Heat to boiling and pass H_2S to ensure complete pptn. of Cu-As Group. Centrifuge and collect supernate. Evaporate to dryness the supernate, add 10-15 drops of water. Take 3 drops of the solution and test for phosphate. (If present, it is to be eliminated). Add 2 drops of HNO_3, boil and add 5 drops of 20% NH_4Cl. Add a piece of litmus paper and add 4*N*-ammonia solution till just alkaline. Centrifuge.

Precipitate or residue
Fe Group—Fe, Cr, Al

Supernate solution
Boil and pass H_2S and centrifuge.

Precipitate or residue
Zn Group—Zn, Mn, Ni, Co

Supernate solution
Mg

Collect the residue, and mix it with 5 times the weight of Na_2CO_3; stir with spatula; transfer to a nickel lid, and fuse in Ni-spoon until a clear melt is obtained (2 minutes of heating on flame would suffice). Cool the melt and drop into water contained in a 10 ml. beaker; boil for 1 minute, scrap the residue from the spoon into the solution, wash the ppt. of carbonates so obtained with hot water, and reject the washings.

Dissolve the carbonate ppt. in hot $4N$-acetic acid. Divide the solution in portions and test a small portion with 5% K_2CrO_4 solution. If yellow ppt., then Ba is present; add more K_2CrO_4 till 2 drops in excess; the solution becomes orange. Warm, stir and let it stand for 5 minutes to ensure complete precipitation. Centrifuge. Decant the supernate to a clean 30 ml. beaker. Stir the precipitate with 2 ml. of water. Centrifuge and discard this washing.

Calcium Group—Ca, Sr, Ba.

Wash the residue of this group containing sulphates of Ca, Sr and Ba with alcohol containing one drop of $4N$—H_2SO_4; centrifuge and discard the washings.

Test a portion of the residue with platinum wire. (Usual flame colours: Ba—green, Sr—deep crimson, Ca—impersistent red.) Take the residue and boil with $2M$—ammonium acetate, centrifuge and separate the supernate.

<table>
<tr>
<td rowspan="2">Residue—$BaCrO_4$
(i) Wash the resdue with $4N$-HCl and test with Pt wire. Green flame —Ba.
(ii) Test the resdue with 1 drop of HCl; place on filter paper, then add one drop of 0·2% sodium rhodizonate (fresh solution). Bright red colour —Ba.</td>
<td colspan="2">Supernate—(Sr and Ca plus K_2CrO_4 etc.)
To it, add $4N$-ammonia till alkaline; now add 2 ml. of ammonium sulphate $(NH_4)_2SO_4$ warm and let stand for 5 minutes: White ppt. of Sr and Ca (mixed).

Wash the ppt. with hot water and reject washings. Treat the ppt. with $4N$ acetic acid and boil for a few minutes to expel CO_2; cool and make alkaline with $4N$-ammonia. Add at least an equal volume of saturated $(NH_4)_2SO_4$. Heat to boiling and let stand for 5 minutes. Centrifuge.</td>
</tr>
<tr>
<td>Residue—$SrSO_4$.
Test with Pt wire: Crimson persistent flame —Sr.</td>
<td>Supernate—$CaSO_4$ (a double salt with ammonium sulphate).
Divide in two.
(i) Add a few drops of ammonium oxalate, warm and let stand for 2-5 minutes: White ppt.—Ca.
(ii) Add to the second portion solid ammonium chloride till saturated; then add 5 drops of 5% potassium ferrocyanide: Yellow ppt· Ca confirmed</td>
</tr>
</table>

Take the residue containing copper and arsenic groups (sulphides). Wash the residue with H_2S water containing 5 g. of ammonium chloride per 100 ml. Reject the washings. Add to the residue to 2 ml. of $N/2$ KOH and heat, then cool and centrifuge.

Residue	*Supernate*
Cu—Group Hg, Bi, Cu, Cd.	As—Group. As, Sb, Sn

Copper Groups.

Wash the residue with water; add 0·5 ml. of 1.5N HCl, stir and transfer to a test tube. Complete the transference of the residue with more acid (say 2 ml.). Boil for 100 seconds and centrifuge.

<table>
<tr>
<td colspan="3">Residue→(black)
Hg, Bi, Cu. Wash with water twice; add 1 ml. 4N-HNO_3; boil and centrifuge.</td>
<td rowspan="3">Supernate: Cd—
Boil off H_2S from the solution; and 4N NaOH in excess, warm and centrifuge: Residue Cd $(OH)_2$; discard supernate.
Wash the ppt. with 5 drops of 20% ammonium chloride; warm gently, dissolve and test for Cd in solution:
(i) Pass H_2S to one portion —Yellow ppt. Cd.
(ii) Cadion test—Slightly acidify with 4N-HCl; add 2 drops of cadion reagent (p-nitrobenzene-diazo→amino-benzene); add excess of N-Alc.KOH→ Pink colour—Cd.
(iii) Make the third portion ammoniacal with 2 props of ammonia; add one drop of thiosinamine reagent and warm gently. Yellow ppt. Cd.</td>
</tr>
<tr>
<td rowspan="2">Residue
HgS, (black) +sulphur (S°).</td>
<td colspan="2">Supernate
Bi, Cu Add conc. ammonia in excess : boil and centrifuge.</td>
</tr>
<tr>
<td>Residue
$Bi(OH)_3$.</td>
<td>Solution
Cu (Blue) complex.</td>
</tr>
</table>

Test for mercury—Add to the residue 3 ml. of N-HCl and 1 ml. of 6 N-HNO_3. Transfer to a beaker and boil down to 2 ml. Transfer back to a tube. Centrifuge. Decant the supernate to a clean tube and discard any residue (which may be sulphur, S°). Divide supernate into 2 parts—

(i) To the supernate add 5 ml. of 0·5M $SnCl_2$ in a tube. A white or greyish ppt.—*Hg*.

(ii) Of the second part, take 2 drops. To it, add 2 drops of 0·05% acetone solution of p-dimethyl benzyl rhodanine and 5 drops of saturated solution of Na-acetate. Pink colour —*Hg*.

Test for bismuth—(i) Dissolve a part of the precipitate of $Bi(OH)_3$ in a few drops of 4 N HNO_3. To the solution, add 2 drops of 10% thiourea solution—Yellow colour—*Bi*.

(ii) Dissolve another part of the precipitate of Bi $(OH)_3$ in a minimum quantity of 4N—HCl; and pour into freshly prepared sodium stannite ($SnCl_2$+excess NaOH)—Black ppt.—*Bi*.

(iii) Dissolve the third part of Bi $(OH)_3$ in a minimum of 4N-HCl; add two drops of 1% solution of alcoholic dimethyl-glyoxime, and make ammoniacal: Yellow ppt.—*Bi*.

Test for copper—(i) Acidify a few drops of the ammoniacal solution of copper salt with 4N-acetic acid ; add a few drops of 5% potassium ferrocyanide: Reddish brown ppt. or colour—*Cu*.

(ii) Place 1 drop of ammoniacal Cu solution of the spot paper; add to it 1 drop of 5% alcoholic solution of cupron (α-benzoin-oxime): Green colour—*Cu*.

Arsenic Group: As, Sb, Sn.

To the solution of arsenic group, add 4N-HCl (avoid adding a large excess of HCl) ; centrifuge and wash with H_2S water containing ammonium chloride. Reject washings; add to the precipitate 1—1·5 ml. of 8N-HCl. Boil for 5 seconds and pass H_2S. Now centrifuge.

<table>
<tr><td rowspan="2">Residue
As</td><td colspan="2">Supernate—Sb,Sn.
Boil off H_2S gas ; add N-KOH drop by drop till any ppt. formed just re-dissolves ; now add Br-water till the solution becomes yellow ; add solid ammonium chloride (a pinch), boil for 2 minutes. Centrifuge.</td></tr>
<tr><td>Residue—$Sn(OH)_4$</td><td>Supernate : Sb.
Add more of NH_4Cl solid, and boil to ensure the removal of all Sn ; acidify with HCl and pass H_2S : Orange ppt.—Sb.</td></tr>
</table>

Test for arsenic—Add to the residue from above 4 ml. of 6*N*-ammonia, and 3 ml. of 3% hydrogen peroxide. Heat to boiling ; centrifuge. Decant the supernate to a clean tube. Discard any residue. Divide the supernate into several portions.

(i) To one portion, add 3 ml. of magnesia mixture ; cool and stir vigorously. A white ppt. of $Mg(NH_4)AsO_4, 6H_2O$, indicates *As*.

(ii) Take the other portion, dilute, and boil of the excess ammonia ; cool and add 5 drops of Ag NO_3 solution. Reddish-brown ppt.—*As*.

(iii) Treat the third portion with conc. HNO_3 in excess ; add an excess of ammonium molybdate solution and heat.—Yellow ppt.—*As*.

Test for antimony—(*a*) Dissolve the orange precipitate from above in HCl (conc.) ; boil off H_2S, take a few drops of the solution, and neutralize the acid with 6*N*-ammonia : add one drop of ammonia in excess, then add about 5 drops of acetic acid, and heat to boiling. Add a crystal of sodium thiosulphate to the hot solution—Bright red ppt.—*Sb*.

(*b*) Take 2 drops of the supernate solution on a spotplate, add a minute crystal of $NaNO_2$, stir and add 2 drops of rhodamine-B reagent.—Violet coloration—*Sb*.

Test for tin—(Stannous and stannic)—Dissolve the residue of stannic hydroxide, $Sn(OH)_4$, in hydrochloric acid. Divide into 4 portions.

(i) To one portion, add a piece of an iron wire and boil for 10-15 seconds ; cool, and decant the clear solution. Add to it one drop of $HgCl_2$—White or grey ppt.—*Sn*.

(ii) Take one drop of the second portion on a filter or test paper; add one drop of saturated solution of cacothelin. Lavender colour (violet or red).—*Sn.*

(iii) Take 4-5 drops of the portion; add 4 drops of 30% tartaric acid solution; and 5 drops of water; then 6 drops of 1% benzoyl phenyl hydroxylamine in 5% acetic acid : White ppt.—*Sn.*

(iv) Take solid residue of $Sn(OH)_4$; dissolve it in conc. HCl; place a little zinc and perform flame mantle test, round a test tube filled with water.

Iron Group : Fe, Cr, Al.

Wash the mixed precipitate of the hydroxides of iron, chromium and aluminium with water ; add 2 or 3 drops of 4*N*-NaOH and 4-5 drops of water ; wash and centrifuge.

<table>
<tr><td colspan="2">Residue
Fe, Cr—Wash the ppt. with 1 ml. of water containing 4N-NaOH ; reject washings. Treat the residue with 2-3 drops of 4N-NaOH+5-6 drops of 20% vol. H_2O_2. Boil for 1 minute and centrifuge.</td><td rowspan="2">Supernate
Al as $NaAlO_2$</td></tr>
<tr><td>Residue—Fe as Fe $(OH)_3$.</td><td>Supernate—Cr as Na_2CrO_4</td></tr>
</table>

Test for iron—Dissolve the precipitate of $Fe(OH)_3$ in 4*N*-HCl.

(i) Take 2 drops of this solution ; add to it 1 drop of ammonium thiocyanate : Blood-red colour—*Fe.*

(ii) To another a few drops of the solution, add a drop of $K_4Fe(CN)_6$ solution : Deep blue colour or ppt.—*Fe*

Test for aluminium—Acidify the solution of $NaAlO_2$ with *N*-HCl ; then make the solution strongly alkaline with ammonia; add to it one drop of *aluminon* (aurin tricarboxylic acid) : Rose red ppt.—*Al*.

Test for chromium—(i) Acidify the solution of Na_2CrO_4 with 4*N*-acetic acid, and add 2 drops of lead acetate solution: Yellow ppt.—*Cr.*

(ii) Acidify the solution of Na_2CrO_4 with $4N$-H_2SO_4 ; cool thoroughly under running water ; add 1 drop of 20% vol. of H_2O_2 ; add 0·5 ml. of a mixture of butyl alcohol and ether; then shake the tube from side to side. Blue top layer—*Cr*

Zinc Group : Co, Ni, Zn, Mn.

Wash the precipitate of sulphides of cobalt, nickel, zinc and manganese obtained by passing hydrogen sulphide in the ammoniacal solution of the supernate of Iron Group, with ml. of water and reject washings ; add to the precipitate 2-5 drops of conc. HCl and 2-3 drops of conc. HNO_3 ; warm, dissolve and transfer to a porcelain dish. Evaporate to dryness over a small flame. To the residue so obtained add 1·5 ml. of N-acetic acid. Heat to boiling ; transfer the solution to a test tube and pass H_2S gas and centrifuge.

<table>
<tr>
<td rowspan="2">Residue—ZnS
Wash and dissolve in a few drops of $4N$-H_2SO_4 ; dilute with a little water; boil off H_2S, and test for Zn in this solution. Divide into 2 portions.</td>
<td colspan="2">Supernate—Sulphides of Mn, Co, Ni. Transfer the solution in a test-tube ; boil off H_2S ; make it just alkaline with conc. ammonia ; add a few drops of Br-water; boil and centrifuge.</td>
</tr>
<tr>
<td>Residue—MnO_2.</td>
<td>Supernate : Ni, Co.
Divide into two portions. Test one portion for Ni. Acidify the second portion with $4N$-HCl and test for Co and Ni.</td>
</tr>
</table>

Test for zinc—(i) To a part of the zinc solution in sulphuric acid, add 1 drop of $K_4Fe(CN)_6$ solution : White ppt.—*Zn.*

(ii) Concentrate the other part of the same zinc solution; add 2 drops of 0·1% copper sulphate solution and 2 drops of ammonium mercury thiocyanate, $[NH_4 \cdot Hg. (SCN)]$—Violet ppt.—*Zn.*

Tests for manganese—(i) Dissolve the black residue (MnO_2) in 0·5 ml. of $4N$-HNO_3 and 2 drops of 20 vol. H_2O_2. Boil till all oxygen evolved out ; cool ; add 0·25 g. of solid sodium bismuthate, Na_3BiO_3. ; centrifuge : Purple colour or violet—*Mn.*

(ii) Dissolve the black residue of MnO_2 in a few drops of $4N$-H_2SO_4 ; add 1 drop of $AgNO_3$ and a little solid ammonium persulphate ; heat to boiling : Pink colour of $KMnO_4$—*Mn*.

Test for nickel—Take 2 drops of the mixed solution of Ni and Cu ; add 2 drops of 1% alcoholic solution of dimethyl glyoxime; add $4N$-ammonia, until alkaline, and warm : Red ppt.—*Ni*.

Test for cobalt—(i) Take 3-4 drops of cobalt solution ; add 1 drop of $SnCl_2$ solution, and mix 0·25 g. of solid ammonium thiocyanate and 1 ml. of normal butyl alcohol dissolved in ether. Shake the test tube from side to side : Blue colour in top layer—*Co*.

(ii) If Ni absent, add to a portion of the solution $4N$-NaOH till just alkaline ; just acidify now with $4N$-HCl ; now add 2-3 drops of 0·5% solution of nitro-R-salt (α-nitroso β-naphthol), followed by 0·5 ml. $4M$-sodium acetate : Red colour—*Co*.

(iii) If Ni present, precipitate out all nickel with demethyl glyoxime ; reject the residue and carry out the test (ii) for Co in the solution.

Magnesium.

Test for Mg in the supernate after removing the sulphides of the Zinc Group. Some tests may be made in the original solution also.

If the solution is acidic or neutral, add $6M$-ammonia solution, till alkaline and then add 2 ml. of ammonia in excess.

(i) Add 2 ml. of 1-M diammonium hydrogen phosphate to the above alkaline solution. Cool the test tube under running water, stir and scratch the tube with a glass rod. Let stand for about 5 minutes. White crystalline ppt. : *Mg*.

Wash this precipitate with 1 ml. of water containing 4-5 drops of $6M$-ammonia. Centrifuge and discard the supernate.

To the precipitate add 1 ml. of water and 5-10 drops of $6M$-HCl. Stir and warm to dissolve.

Now add 1 drop of p-nitrobenzene-azoresorcinol (*magneson*) solution and 5 ml. of $2M$-NaOH : Sky-blue ppt.—*Mg*.

Sodium and Potassium

Use 4 ml of original unknown solution in case all groups (Ag Group to Zinc Group) are absent, or the remaining two-thirds of the solution left after the separation of the Zinc Group.

Add conc. ($15N$) nitric acid, little by bittle, with stirring, until the solution is acidic; then add 5 ml. of conc. HNO_3 in excess. (If the solution is alkaline or neutral, add 5 ml. of conc. HNO_3).

Place this solution in an evaporating dish, and evaporate to dryness. Heat the dish on direct flame with the hottest flame possible for 5-10 minutes; thus volatilise all ammonium salts.

Cool the dish thoroughly ; add 5 ml. of water and 1 ml. of 6*N*-acetic acid. Stir, warm slightly, decant to a test-tube and centrifuge. Perform flame test for Na and K with this solution. Divide the supernate into equal portions in two tubes.

Portion 1—Test for sodium.—Add 4 ml. of magnesium uranyl acetate solution. Scratch and stir thoroughly : Light yellow crystalline ppt. of [Na. Mg $(UO_2)_3$ Ac_9]—*Na.*

Portion 2—Test for potassium. Add 4 ml. of sodium cobaltinitrite solution. Stir and let stand for 5 minutes. Yellow ppt. of $K_2 . NaCo (NO_2)_6$—*K*.

Acid Insoluble Substances.

The following substances do not dissolve appreciably in acids :—

1. Free elements C, S, Si.
2. Certain lead salts—$PbSO_4$, $PbCrO_4$ (ignited).
3. Silver salts—AgCl, AgBr, AgI, AgCN ; $Ag_3 Fe (CN)_6$, $Ag_4 Fe (CN)_6$.
4. Sulphates—$BaSO_4$, $SrSO_4$ ($CaSO_4$ is slightly soluble in water).
5. Chromium salts—$CrCl_3$, $Cr_2 (SO_4)_3$.
6. Ignited oxides—SnO_2, Al_2O_3, Cr_2O_3, Sb_2O_4.
7. Silica and several silicates:
8. Miscellaneous—CaF_2, $Fe_4 [Fe(CN)_6]_3$ (Prussian blue), SiC.

1. *First identify carbon and sulphur*—(If the residue is colourless, omit this step). If it is yellow or black, transfer the dry residue to a porcelain crucible. Heat to redness.

(i) A yellow residue that burns with a blue flame evolving SO_2 smell—*S.*

(ii) A black residue that slowly burns away at red heat, evolving CO_2—*C.*

2. *Then identify $PbSO_4$*—When C and S have been removed as SO_2 and CO_2, the residue contains : $PbSO_4$, AgCl, AgBr, AgI, $BaSO_4$, $SrSO_4$, $CaSO_4$. CaF_2, CrX_3 (anhyd.), [Fe_4 $(CN)_6]_3$, SnO_2, Al_2O_3, Cr_2O_3, Sb_2O_4, SiO_2, Si and silicates.

(i) Take a small portion of the residue and moisten with ammonium sulphide. A blackening indicates the presence of lead and silver compounds. In this case, proceed with the step (ii). If the colour remains unchanged, the ammonium acetate treatment (step ii) and sulphuric acid-zinc treatment may be eliminated. Proceed with the potassium carbonate step (marked with asterisk).

(ii) Transfer the remaining residue to a small beaker. Add 10 ml. of 3 *M*-ammonium acetate and 1 ml. acetic acid. Heat to boiling for 2-3 minutes. Transfer to a test tube and centrifuge. Divide the supernate into 2 portions. Wash the residue twice with water and discard the washings.

Supernate—$PbAc_2$+ammonium sulphate. Divide the supernate into two portions,— (i) Add 3 ml. of *M*-K_2CrO_4 to one portion—Yellow ppt.—*Pb*. (ii) Dilute the second portion with 20 ml. of water. Add 10 ml. of 0·5 *M*-$BaCl_2$; White ppt—SO_4''. This confirms $PbSO_4$.	*Residue*—AgCl, AgBr, AgI, $BaSO_4$, $SrSO_4$, $CaSO_4$, CaF_2, CrX_3 (anhyd.), $Fe_4[Fe(CN)_6]_3$, SnO_2, Al_2O_3, Cr_2O_3, Sb_2O_4, SiO_2, Si and silicates. Residue from (2).

3. Now identify *halides* in the residue from (2)—Transfer the residue from (2) to a beaker. Add 15 ml. of 3 *M* sulphuric acid and a pinch of pure zinc. Warm until the reaction is complete, and then transfer the solution to a test tube and centrifuge. Decant the supernate to a beaker.

Stir the residue with 5 ml. of water, centrifuge and add the washings to the previous supernate.

Supernate—I^-, Br^-, Cl^- (halides) identify them as usual.	*Residue*— Ag°, $BaSO_4$ $SrSO_4$, $CaSO_4$, CaF_2, CrX_3 (anhyd.) Fe_4 $[Fe(CN)_6]_3$, SnO_2, Al_2O_3, Cr_2O_3, Sb_2O_4, SiO_2, Si, silicates. Residue from (3).

4. Now identify *Ag*—Add to the residue from (3) 5 ml. of 6*M*-nitric acid, heat to boiling and centrifuge. Decant the supernate to a tube, and wash the residue with 5 ml. of water, and discard the washings.

Supernate	Residue
Supernate—Ag^+ Test for silver as usual.	*Residue**—$BaSO_4$, $SrSO_4$, $CaSO_4$, CaF_2, CrX_3 (anhyd.), Fe_{-} $[Fe(CN)_6]_3$, SnO_2, Al_2O_3, Cr_2O_3, Sb_2O_4, SiO_2, Si and silicates. Residue from (4).

5. Now identify sulphate $SO_4^{=}$, fluoride F^-, ferrocyanide Fe $(CN)_6^{==}$, X^-, silicate $SiO_3^{=}$.—Transfer the residue from (4) to a beaker; add 15 ml. of 50% K_2CO_3 solution, cover with a watch glass and heat to boiling for 10-15 minutes. Add a little water from time to time to replace any loss in evaporation. Transfer to a test-tube and centrifuge. Decant the supernate to a beaker.

Stir the residue with 5 ml. of water. Centrifuge. Add these washings to the previous supernate.

Supernate	Residue
Supernate—$SO_4^{=}$, F^-, Fe $(CN)_6^{=}$, X^-, $SiO_3^{=}$ Analyse these anions as usual.	*Residue*—$BaOO_3$, $SrCO_3$, $OaCO_3$ Fe $(OH)_3$, Cr $(OH)_3$, SnO_2, Al_2O_3, Cr_2O_3, Sb_2O_4, Si and silicates. Residue from (5).

6. Now identify for Ba^{++}, Sr^{++}, Ca^{++}, Fe^{+++}, Cr^{+++} and Al^{+++}.—Add to the residue from (5) 15 ml. of 6*M*-HCl; heat to boiling and filter. Wash the residue two times with 5 ml. of water. Add these washings to the previous filtrate.

Solution	Residue
Solution—Ba^{2+}, Sr^{2+}, Ca^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}—Analyze 10 ml. portion for the cations as usual in the analysis.	*Residue*—SnO_2, Al_2O_3, Cr_2O_3, Sb_2O_4, SiO_2, Si, silicates. Residue from (6).

7. Convert now this residue to *suitable cations* and *anions* for regular analysis: Collect the residue from (6) and place the filter paper and the residue in a nickel crucible; heat until the filter paper is completely burnt away.

Add about 5 g. of $(Na_2CO_3 + K_2CO_3 + Na_2O_2)$ fusion mixture, stir and heat to redness for 10—15 minutes. Cool the crucible and contents; add a little water and warm to loosen the residue. Transfer to a beaker; add about 30-40 ml. of water and heat to boiling until the residue breaks up completely.

Filter; wash the residue 3 times with water. Discard the washings.

Solution—CrO_4^{2-}, SiO_3^{2-}, AlO_2^-; $HSnO_3^-$, SbO_3^{3-}.	*Residue*—Al $(OH)_3$, $Sn(OH)_4$, $Sb(OH)_3$, $CaCO_3$ etc.
(*i*) Test for chromate and silicate in two separate 5 ml. portions. (ii) Acidify the remaining solution with 6*M*-HCl. (iii) Mak alkaline with 6*M*-ammonia. Filter off any residue and discard the filtrate. (iv) Dissolve the residue by heating with 15 ml. of 6*M*-HCl. Combine this solution with the hydrochloric acid solution of the residue. Test for cations in it as usual.	(i) Add 15 ml. of 6*M*-HCl; heat to boiling for 2-3 minutes. Centrifuge. Continue this with the hydrochloric acid solution of the fusion step (iv); use a 5-10 ml. portion for analysis of cations.

Analysis of Anions

Group I—This group consists of anions which get precipitated from a *sligtly basic* solution; the precipitant is a mixture of *calcium nitrate* and *barium nitrate*: The anions of this group are—

Sulphate	Carbonate	Phosphate	Borate
Sulphite	Silicate	Arsenite	Oxalate
Thiosulphate	Chromate	Arsenate	Fluoride

Tartrate is only slowly precipitated in this group, hence it is mainly taken up in Group III.

Thio-sulphate comes both in Group I (as calcium thiosulphate) and Group II (as silver sulphide). The sulphate and chromate ions are best precipitated as barium salts; the others of this group as calcium salts.

Group II—The precipitant is *silver nitrate* in a *dilute nitric acid* solution. The anions of the group are—

Chloride	Cyanide	Thiosulphate
Bromide	Ferrocyanide	
Iodide	Ferricyanide	
Sulphide	Tniocyanate	

Group III—The anions not precipitated in Groups I and II belong to this group :—

Nitrate	Acetate	Permanganate
Nitrite	Tartrate	Borate (sometimes)
Chlorate	Citrate	

There is no systematic way of separation of anions as is of cations. A series of general tests are convenient. In the following description, we presume that the anions are present as *sodium* and *potassium* compounds only. Other cations may interfere in the analysis of anions, and hence they must be removed.

The coloured anions are: chromate, dichromate, ferricyanide, ferrocyanide and permanganate. A colourless solution need not be tested for these anions.

Na or K salts of anions

| $Ba(NO_3)_2 + Ca(NO_3)_2$ mixture (slightly basic). Centrifuge

Residue Group I

Supernate (Groups II+III)

| Add $AgNO_3$ and acidify with dil. HNO_3 in exeess; centrifuge.

Residue Group II

Supernate (Reject)

Group III anions should be tested with separate portions of the unknown.

Reducing ions—Any anion which reduces in acidic solution (*i.e.*, in presenee of dil. H_2SO_4) a solution of *potassium permanganate* (a drop or two of 0·01 *M*) is regarded as a reducing ion.

Reduction of acidified $KMnO_4$ in cold immediately.

Sulphite	Tartrate	Thiocyanate.
Thiosulphate	Citrate	Cyanide
Sulphide	Iodide	Ferrocyanide
Arsenite	Bromide	Nitrite.

Oxalates reduce this solution slowly; the solution must be heated to initiate the reaction.

Oxidizing ions—Any anion which liberates free iodine from an acidified solution of *potassium iodide* is known as an oxidizing ion. Such a reaction mixture is shaken with carbon tetrachloride layer (violet colour). The ions of this category are:

Chromate	Chlorate
Dichromate	Nitrite
Ferricyanide	Permanganate.

The anions as nitrate and arsenate oxidize only when present in high concentrations.

Volatile substances—Upon acidification, the following anions evolve gaseous substances (add dil. H_2SO_4 and warm):

Carbonate—CO_2	Sulphide—H_2S
Sulphite—SO_2	Cyanide—HCN.
Thiosulphate—SO_2	Nitrite—NO,NO_2.

Group I

1. First test for *silicate*—Add 1 ml. of 6*N* conc. HCl to 1 ml. of the unknown solution in a smal beaker. Stir. If much silicate is present, a gel of silicic acid is immediately formed. Evaporate the mixture to dryness and continue to heat the residue for 5 minutes. Cool the residue, and add 1 ml. of 6*N*—HCl and 5 ml. of water. Gummy insoluble residue: *silicate*; centrifuge, and remove this residue. Keep the supernate for the test of sulphate etc. (In presence of fluoride ions, silicate ion is volatilized as SiF_4).

2. Now test for *sulphate*—To the supernate, add $BaCl_2$ (1 ml. of *M*-$BaCl_2$)—Fine white ppt.—*sulphate.*

Now test for *sulphite*, *sulphide* and *thiosulphate*:—

(i) *Sulphide*—Take 2 ml. of the unknown in a test tube; add 6 *M* ammonia solution to make it just basic. Add 2 ml. more of ammonia solution; stir and add 2 ml. of 0·5*M*-tetramine zinc nitrate solution. If no white ppt.—*sulphide absent.*

If a white ppt., centrifuge, decant the supernate to a clean test-tube and in it test for sulphite and thiosulphate.

Stir the ppt. with 2 ml. of water, centrifuge and discard the supernate.

Add 2 ml. of 6 *M*-HCl to the ppt., warm and test for sulphide with lead acetate paper over the mouth of the test tube: Black stain—Sulphide.

Sulphite—To the supernate from the sulphide operation, add 3 ml. of saturated strontium nitrate solution. Stir thoroughly. Let stand for 10 minutes. Centrifuge.

Decant the clear supernate to a clean test-tube and reserve the supernate for thiosulphate test.

Stir the residue with 2 ml. of saturated strontium nitrate solution. Centrifuge and discard the washings.

Stir the residue with 1 ml. of water; add 1 ml. of 6*M*-HCl and 1 ml. of *M*-$BaCl_2$ solution. Stir and centrifuge off any residue.

Decant the supernate to a clean test tube. Add iodine-potassium iodide solution (or bromine water) till just yellow: Fine white ppt.—*Sulphite*.

Thiosulphate—To the supernate from the sulphite operation add 6 *M*-HCl till acidic.; warm: white turbidity of sulphur—*thiosulphate*.

Sulphate, sulphide, sulphite and thiosulphate

To *acidic* solution, add $BaCl_2$
Centrifuge

- White residue *Sulphate*
- Sulphide, sulphite, thiosulphate
  add NH_4OH excess + Tetrammine Zn nitrate
  - White residue of ZnS
    Sulphide:
    HCl and warm
    H_2S
    Test with $PbAC_2$ paper. Black stain—*Sulphide*.
  - Sulphite + thiosulphate
    add saturated $Sr(NO_3)_2$
    - White residue
      Sr Sulphite
      add 6*M*-HCl and centrifuge
      - *Residue*
        Discard
      - *Supernate*
        KI_3 or Br_2 water
        White ppt.—*Sulphite*.
    - *Supernate*
      Thiosulphate
      add 6*N*-HCl and warm
      White turbidity of sulphur—*Thiosulphate*

Test other anions of Group I as in the usual anlysis.

Group II

Ferricyanide—To 1 ml. of the unknown, add 6*N*-HCl in excess and then 1 ml. of fresh *M*-$FeSO_4$ solution : Deep blue colour or ppt.

(Turnbull's Blue)—Ferricyanide.

Ferrocyanide, and thiocyanate—To 0·5 ml. of the unknown, add 6*N*-HCl in excess and then 1 ml. of 0·5 *M*-$FeCl_3$:

Deep blue colour or ppt.—Ferrocyanide.

Blood red solution—Thiocyanate.

If both are present, stir the above mixture and put 1 drop of it on the centre of a dry filter paper. The red solution will spread, forming a red ring ; and leaving a blue spot in the centre.

Test other anions of this Group II as usual.

Group III

Nitrite—Put about 1 ml. of the unknown in a test tube. Add 1 ml. of fresh $FeSO_4$ solution. Centrifuge and discard any precipitate. Add another 1 ml. of $FeSO_4$ solution and acidify with 6*M*-acetic acid: A deep brown colour (which disappears on warming)—*Nitrite.*

If a nitrite is present, nitrate test may be omitted.

Nitrate—Perform the usual ring test with $FeSO_4$ and conc. H_2SO_4. (First add to the unknown a slight excess of Ag_2SO_4 solution to precipitate the halides. Centrifuge and remove the ppt. of silver halides. Test for nitrate in the supernate).

Chlorate—Take 1 ml. of unknown in the test blue. Add 6*M*-nitric acid with stirring till acidic. Now add 0·5 *M*-$AgNO_3$, drop by drop, till the precipitation is complete. Add 5 drops of $AgNO_3$ further. Centrifuge off the ppt., and decant the supernate in a clean test tube. Now add 3 drops of 6*M*-KNO_2 and 2 ml. of 6*M*-HNO_3, and heat to boiling. Curdy white ppt.—*Chlorate.*

PART V

Simple Gravimetric Analysis

Some operations :—Gravimetric analysis involves the following operations :—

(1) Solution.
(2) Precipitation.
(3) Washing and filtration.
(4) Drying.
(5) Ignition.
(6) Weighing.

(1) *Solution*—In case the substance to be estimated gravimetrically is not given in the form of a solution, weigh out exactly a suitable quantity (which may give about 2·25 g. of the ignited precipitate) and dissolve it in about 50 ml. of distilled water or acid in a clean beaker.

(2) *Precipitation*—In precipitating insoluble compounds, we aim at securing coarse, granular and dense precipitate, as far as possible, so that it may not pass through the filter paper. This can be achieved by (*i*) adding the precipitating solution (known as a *precipitant*) drop by drop so that the solution does not become supersaturated from the very beginning ; (*ii*) stirring constantly when the precipitant is being added so that crystals formed come in contact with the supersaturated solution and solid is deposited round them, (thus crystals become bigger in size and new ucleiare not formed) ; adding a hot solution of the precipitant to the boiling solution so that the solubility is maximum at the time of precipitation and surface energy minimum and (*iv*) adding some electrolyte to avoid colloid formation, specially during washing.

The best results can, therefore, be obtained as follows :—

Heat the solution to boiling and add to it gradually drop by drop with constant stirring a heated solution of the precipitant. Allow it to stand till the precipitate settles down. Now add a few more drops of the precipitating agent with the help of a glass rod such that they come in contact with the clear supernatant liquid. If no turbidity is produced, the precipitation has been complete. If, however, further precipitation occurs, add more of the precipitant and proceed like this till addition of the precipitant does not produce turbidity any more with supernatant liquid.

(3) *Washing and filtration*—Fit up a gravimetric filter paper (the weight of ash of which is known) to a funnel. See that it fits in closely and there is no air bubble between the funnel and the filter paper. This is done by properly adjusting the folds of a filter paper in coherence with the solid angle of the funnel. Moisten the filter paper with distilled water and press it against the sides of the funnel so that it fits tightly within the funnel.

Washing by decantation—The precipitates are best washed in the beaker itself by decantation. Add hot distilled water to the precipitate, about 20 ml. at a time, shake, allow it to stand and decant off the clear liquid through the filter paper. This should be done three or four times, till the precipitate is almost free from certain specified ions.

The precipitate should now be transferred to the filter paper either directly or with a stream of water from a wash bottle. When almost the whole of the precipitate has been transferred to the filter paper, the sides of the beaker should be gently rubbed with a "policeman," which is a glass rod tipped with about quarter of an inch of smooth rubber tubing. This would remove the precipitate sticking to the sides of the beaker. The beaker and glass rod should now be washed again and the entire washing passed through the paper. Continue washing of the precipitate till the filtrate gives no test for the ion which has to be removed. *During washing and transferring of the precipitate, it should be remembered that the liquid does not rise beyond about 3/4 of the filter paper cone.* While washing the precipitate, the jet of water should be directed at the top of the paper and the funnel should be rotated by hand when the jet is playing. "If you wash the top of the paper, the precipitate will look after itself." It is much more efficient to wash four times, quarter-filling the funnel each time than to wash once completely filling the funnel.

(4) *Drying*—Cover the funnel with a piece of paper having a few small holes to enable water vapours to escape during drying, and put it either in a steam oven or over a chimney consisting of a truncated iron cone. In the latter case, apply a small adjusted flame from the side of the wire gauze so that drying occurs only by freely circulating heated air. Dry as thoroughly as possible in this way.

(5) *Ignition*—When the precipitate is dried, transfer as much of it as possible with the help of a feather, to a clean and dry clock glass placed over a glazed paper and cover with a funnel. Now fold the filter paper several times till it looks like a long cone. Catch the top side (to which no precipitate is sticking) with a pair of tongs and kindle it by the flame of a horizontally-held Bunsen burner. Let the ash collect inside the crucible. Any particle that has fallen over the glazed paper is also transferred to crucible by means

of a feather. The crucible is now heated over a clay pipe triangle till the whole carbon disappears leaving a clear ash.

During this process, some of the precipitate gets reduced by means of the carbon of the filter paper. This is brought to the original state by using suitable reagents. After this, the crucible is cooled and the precipitate is transferred to it by means of a feather. The crucible is now heated over a claypipe triangle to a constant weight according to the given directions.

(6) *Weighing*—Subtracting the weight of the empty crucible from the constant weight of the crucible along with the precipitate, we get the weight of the precipitate and ash. The weight of ash of a gravimetric filter paper is known. This is subtracted from the final weight.

Precaution in Weighing.

The student is already familiar with the use of a chemical balance. He ought to have practice of accurate and speedy weighing. There are different makes of balances, Bunge, Sartorius, and others with slight technical differences. Though the student is to use the balance allotted to him throughout the session, he ought to familiarize himself with other types also. The following precautions will be helpful.

(*i*) A weighing should not take more than 3—5 minutes; when a known amount of substance has to be weighed, the period should not exceed beyond 7 minutes. The quickness can be achieved by placing the weights in a regular order, rather than speculative.

(*ii*) See that the weights are properly placed in the weight box. The only place for the weights is either on the pan of the balance or in the weight box.

(*iii*) Learn the proper use of rider. The weight of the rider is 0·01 gram (10 milligrams). The balance is usually adjusted without the rider on the beam; or by placing the rider at Zero (if Zero is in the centre of the beam. In some cases, the Zero is at one extreme end of the beam. In such cases 5 milligram riders are used), and if you are provided with the usual 10 mg. rider; regard the graduation 5 on the beam as your Zero, then 6 becomes 0·002 and 7 is 0·004, 8 is 0·006, 9 is 0·008 and 10 is 0.01 and smaller divisions have corresponding values.

(*iv*) Do not disturb the adjustments of the balance without consulting your partners on the balance. They might have taken a part of the weighings, and shall be taking other weighings on the same balance.

(*v*) Do not weigh a substance hot, unless it has been brought to the room temperature in a desiccator.

(*vi*) Weigh with a steady hand.

1. Estimation of Iron as Oxide in a Solution of Ferrous Ammonium Sulphate.

Reactions—Iron is precipitated as hydrous oxide on the addition of ammonium hydroxide to a ferric salt solution. Ferrous salts are first converted to ferric by heating them with nitric acid :—

$$2FeSO_4+H_2SO_4+O=Fe_2(SO_4)_3+H_2O$$
$$Fe_2(SO_4)_3+6NH_4OH=2Fe(OH)_3+3(NH_4)_2SO_4$$

The hydrous oxide is finally ignited to ferric oxide :

$$2Fe(OH)_3=Fe_2O_3+3H_2O.$$

Solution—The solution supplied has been prepared by dissolving about 125 g. of ferrous ammonium sulphate per litre; 10 ml of this solution will yield 0·25 g. of Fe_2O_3. Each solution thus for estimation should contain about 1·25 g. of ferrous ammonium sulphate. A little sulphuric acid is added to the solution to prevent hydrolysis.

Process—To the given solution for estimation, add about 20 ml. of distilled water and heat the solution to boiling. Add about 1 ml. of concentrated nitric acid to the hot solution and again heat. At first, a brownish colour is obtained, which on heating turns yellow. When all ferrous has been converted thus to ferric (this can be known by experience), add to the boiling solution an excess of ammonium hydroxide solution, and stir well. The solution should markedly smell of ammonia. Now allow the precipitate to settle. Wash the precipitate 3—4 times by decantation using hot water (decantation should be done through the filter paper). When almost free from sulphate (test with barium chloride solution), transfer the precipitate to the filter paper (see that the precipitate does not go beyond two-thirds of the cone of the filter paper). Wash the precipitate again on the filter paper with hot water till completely free from sulphate.

When the filtrate has trickled out completely, cover the funnel with a clean paper with punctured holes for vapours to pass out, and transfer it to the chimney for drying. When the precipitate has completely dried (as seen by characteristic appearance), separate it cautiously on a clock glass placed on the glazed paper. Cover the precipitate with an inverted dry funnel. Fold the filter paper to form a small thin cone, and kindle it by a Bunsen flame held horizontally in the hand. Allow the ash to collect in a previously heated and weig hed crucible. Transfer carefully the particles from the glazed paper also to the crucible. Heat the ash till carbonaceous portion has completely burnt out. Cool the crucible, add a drop of concentrated nitric acid and heat gently and then strongly.

Cool the crucible, and transfer the precipitate to it and again heat to a constant weight.

$$2Fe \equiv Fe_2O_3 \equiv 2FeSO_4 . (NH_4)_2SO_4.6H_2O.$$

$2 \times 55.84 = 111.68$ 159.68 $2 \times 392.13 = 784.26.$

Weight of $Fe_2O_3 \times 0.6994 =$ Weight of iron.

Weight of $FeSO_4.(NH_4)_2SO_4.6H_2O \times 0{\cdot}1424 =$ Weight of Fe.

Weight of $Fe_2O_3 \times 4{\cdot}911 =$ Weight of $FeSO_4.(NH_4)_2SO_4.6H_2O$.

Alternate method—Precipitation of iron with cupferron—This reagent is the ammonium salt of N-nitroso-N-phenyl hydroxyl-amine. It precipitates iron completely in strong mineral acid solutions (hydrochloric or sulphuric). It also precipitates copper from faintly acid solutions (since it could precipitate copper and iron both, hence its name *cupferron*). A freshly prepared 6 per cent aqueous solution of the reagent should be used.

Procedure—Oxidise the given ferrous ammonium sulphate solution with 1 ml. of concentrated nitric acid and heating. Precipitate the ferric iron as hydroxide by adding an excess of ammonia. Re-dissolve the precipitate in an excess of strong hydrochloric acid (or sulphuric acid). Cool the solution (10°), and add a freshly prepared 6% solution of cupferron slowly with constant vigorous stirring of the contents, until no further formation of brown precipitate takes place. (The formation of a white precipitate of nitrosophenylhy droxylamine indicates that the reagent has been added in excess). Filter out the precipitate immediately, was h several times with 10 per cent (by volume) of hydrochloric acid containing 1. 5 g. of cupferron per litre, and finally with water. Ignite the precipitate with paper in a silica crucible, and weigh as Fe_2O_3.

2. Estimation of Copper as Cupric oxide in a Solution of Copper Sulphate.

Reactions—The given solution of copper sulphate is precipitated as cupric hydroxide by hot caustic alkali, and then ignited to cupric oxide.

$$CuSO_4 + 2NaOH = Cu(OH)_2 \downarrow + Na_2SO_4.$$
$$Cu(OH)_2 = CuO + H_2O.$$

Solution—The solution usually given for estimation is of copper sulphate (78 g. per litre). 10 ml. of this solution (containing 0.78 g. of the salt) would give about 0.25 g. of the precipitate. A few drops of sulphuric acid are added to the solution to prevent hydrolysis.

Process—Take the given solution for estimation in a beaker, add about 20 ml. of water and heat the contents to boiling (the

beaker is covered with a clock glass before applying heat to prevent loss by spurting). Boil separately a fairly strong solution of caustic soda. Add this to the hot solution of copper sulphate with constant stirring (stirring not by a glass rod, but just by centrifugally rotating the beaker with steadiness); as the alkali has been added in just an excess, the brown precipitate settles down becoming granular. Add a few drops more of alkali, boil the solution and allow the precipitate to settle. Test the supernatant liquid with a tip of the red litmus paper, and see whether the alkali has been added in excess; if not, add a few more drops.

The clear supernatant liquid is now decanted through a well fitted gravimetric filter paper. The precipitate is then carefully transferred to the filter paper, and again washed with boiling water. When completely free from sulphate ions (as tested with barium chloride solution), dry the precipitate on chimney.

When the precipitate has been completely dried, remove it on a clock glass as far as possible, and cover it with an inverted funnel. Spread the glazed paper, and place the crucible in a clean dry porcelain dish, and kindle the rolled filter paper and collect the ash in the crucible. The ash particles from the glazed paper of the dish are also transferred to the crucible. Place the crucible on a clay-pipe triangle and heat. When all carbonaceous matter has disappeared, cool the crucible, and add a drop of concentrated nitric acid; half cover the lid and heat, first gently and then strongly. Cool the crucible.

Transfer the precipitate to the crucible from the clock glass with the aid of a feather. Heat it and weigh; again heat and weigh. Repeat the process till a constant weight has been obtained.

N.B.—The precipitate of cupric oxide sticks to the sides of the beaker. Always keep it covered with water. Do not leave it overnight for filtration.

$$\underset{63.57}{Cu} \equiv \underset{79.57}{CuO} \equiv \underset{249.71}{CuSO_4.5H_2O}.$$

Weight of $CuO \times 0.798 =$ weight of Cu.

Weight of $CuO \times 3.138 =$ weight of $CuSO_4.5H_2O$.

Treatment of the ash—The ash has been treated with nitric acid which converts the reduced oxide to the cupric state. The reduction is effected by the carbon of the filter paper in the course of ignition :

$$2CuO + C = Cu_2O + CO;\ 2CuO + 2C = 2Cu + 2CO.$$

The oxygen provided by nitric acid converts back the metallic copper and cuprous oxide both to cupric oxide.

3. Estimation of Silver as Silver Chloride in a Solution of Silver Nitrate.

Reaction—The given silver nitrate solution is treated with hydrochloric acid in presence of nitric acid. This precipitates the whole of silver as silver chloride.

$$AgNO_3 + HCl = AgCl \downarrow + HNO_3.$$

The chloride is weighed as such.

Solution—The solution supplied is of pure silver nitrate. The silver nitrate is weighed about 28 g. per litre which would give a precipitate of about 0.25 g., if 10 ml. of the solution (containing 0.28 g. silver nitrate) are taken for estimation.

Process—Add to the cold supplied solution about 2 ml. of concentrated nitric acid, and then add a dilute solution of hydrochloric acid with constant stirring. Test the supernatant liquid to ensure the complete precipitation. (Allow the precipitate to settle and see whether the addition of a fresh drop of hydrochloric acid causes any further precipitate or not. If it causes further precipitation, then add more of the precipitant).

Allow the beaker to stand in dark until the precipitate has completely settled. Then decant the liquid through a gravimetric filter paper, and wash the precipitate three times by decantation with water, acidulated with a few ml. of dilute nitric acid (5 ml. per wash-bottle).

Transfer the precipitate to the filter paper and again wash it till completely free from chloride ions (test the filtrate with silver nitrate solution). Now dry the precipitate over a chimney *as completely as possible.*

Transfer the precipitate over a clock glass as far as possible and burn the filter paper for the ash in the crucible in the usual way. Place the crucible on Bunsen flame and ignite the ash as completely as possible: cool the crucible and add to the ash one drop of concentrated nitric acid and one drop of concentrated hydrochloric acid and again heat it carefully.

Now transfer the precipitate into the crucible, half cover the lid and heat the precipitate gently, holding the burner horizontally by the hand and waving. When the mass fuses half, stop heating at this stage. The rest half would fuse by the heat already supplied. Cool the crucible in the desiccator and weigh.

N.B.—The precipitate of silver chloride is not strongly heated. On strong fusion, it is changed to silver that percolates

through the walls of the crucible. A weight taken to be constant at 130° is usually sufficient.

$$\underset{107.88}{Ag} \equiv \underset{143.34}{AgCl} \equiv \underset{169.89}{AgNO_3}$$

Weight of $AgCl \times 0.7526 =$ weight of Ag.

4. Estimation of Chloride as Silver Chloride in a Solution of Potassium Chloride.

Reaction—This estimation is complementary to the one already given. The given chloride solution is acidified with nitric acid and precipitated as silver chloride :

$$KCl + AgNO_3 = AgCl \downarrow + KNO_3.$$

Solution—A potassium chloride solution containing about 12·5 g. of the salt per litre is usually given for estimation. 10 ml. of the solution would give about 0.25 g. of silver chloride precipitate.

Process—Acidify the given solution with a few drops of strong nitric acid. Precipitate silver chloride in cold by adding a slight excess of silver nitrate solution, and stir vigorously all the while, but do not strike against the sides of the beaker with glass rod (the precipitate sticks in the scratches thus produced). Allow the precipitate to settle, and test the supernatant clear liquid with a fresh drop of silver nitrate solution to ensure complete precipitation. Break the clots lightly with glass rod. Wash the precipitate several times with distilled water, acidulated with dilute nitric acid. Transfer the precipitate to the filter paper and wash it several times, till free from silver ions (test the filtrate with dilute hydrochloric acid). Dry the precipitate and separate it from filter paper. Burn the ash and treat it as described above in the estimation of silver. Finally fuse the precipitate gently and weigh as AgCl.

$$\underset{74{\cdot}55}{KCl} \equiv \underset{35.46}{Cl} \equiv \underset{143{\cdot}34}{AgCl.}$$

Weight of $AgCl \times 0{\cdot}2474 =$ weight of Cl.

5. Examination of Barium as Barium Sulphate in a Solution of Barium Chloride

Reaction—Barium chloride solution with dilute sulphuric acid gives a precipitate of barium sulphate which is weighed as such:

$$BaCl_2 + H_2SO_4 = BaSO_4 \downarrow + 2HCl.$$

Solution—The solution supplied is of barium chloride, $BaCl_2 . 2H_2O$, of which usually 25 g. are dissolved for a litre of solution.

10 ml. of this solution (containing 0·25 g. of the crystallised salt) would yield about 0. 25 g. of the precipitate.

Process—To the given solution, add about 20 ml. of water and 5 ml. of dilute hydrochloric acid. Heat the solution to boiling and add to it a hot solution of dilute sulphuric acid with constant shaking or stirring The heavy precipitate quickly settles down. Keep it standing for about 2 minutes and test the supernatant liquid with a drop of dilute sulphuric acid. If the precipitation is complete, wash the precipitate with hot water by decantation through the filter paper till free from chloride ions (test the filtrate with silver nitrate solution) and also free from sulphate ions (test with barium chloride solution). Transfer the precipitate to the filter paper, and again wash with hot water several times. Dry the precipitate on a chimney; and when dried, transfer the precipitate to a clock glass as far as possible and burn the filter paper to a clear ash as usual. Ignite the ash, cool it and add a drop of concentrated hydrochloric acid and a drop of sulphuric acid to the ash. Heat the crucible gently so that the white fumes of sulphuric anhydride are removed (while heating, cover the crucible half with its lid). Heat it now strongly, cool and transfer the precipitate from the clock glass to the crucible and heat to a constant weight.

$$\underset{137.36}{Ba} \equiv \underset{233.42}{BaSO_4} \equiv \underset{244.30}{BaCl_2.2H_2O}.$$

Weight of $BaSO_4 \times 0\cdot5885$ = weight of Ba.

Treatment of the ash—In the course of the ignition of the filter paper, a part of the precipitate is reduced by the carbon of filter paper, forming barium sulphide. Moreover, barium sulphate precipitate carries along with it some barium chloride adsorbed at the surface. Barium sulphide is changed to barium chloride when treated with hydrochloric acid, and it in its turn is changed to barium sulphate when the ash is treated with sulphuric acid :

$$BaSO_4 + 4C = BaS + 4CO.$$
$$BaS + 2HCl = BaCl_2 + H_2S.$$
$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

6. Estimation of Sulphate as Barium Sulphate in a Solution of Potassium Sulphate (or Copper Sulphate, or Ferrous Ammonium Sulphate)

Reaction—A soluble sulphate is precipitated as barium sulphate on the addition of a solution of barium chloride :

$$K_2SO_4 + BaCl_2 = BaSO_4 \downarrow + 2KCl.$$
$$CuSO_4 + BaCl_2 = BaSO_4 \downarrow + CuCl_2.$$

Solution—A potassium sulphate solution is the best for estimation. About 20 g. of potassium sulphate are dissolved per litre; 10 ml. of this solution (containing about 0·2 g. of the salt) would give about 0·25 g. of the precipitate.

If the estimation of sulphate has to be done in a solid sample, one can weigh out about 0·3 g. of copper sulphate or 0.2 g. of ferrous ammonium sulphate for each estimation and dissolve in water, adding about 1 ml. of concentrated hydrochloric acid to the solution.

Process—To the given solution of the soluble sulphate, add 2 ml. of strong hydrochloric acid, and boil. Heat separately a clear solution of 10% barium chloride (the shelf reagent may do) and add the hot solution to the sulphate solution. A thick precipitate of barium sulphate would appear. Do not add the precipitant at a rate faster than 1 ml. per minute in order to prevent the chloride from being carried down with the sulphate. Allow the precipitate to stand for half an-hour. Test the supernatant liquid with a fresh drop of barium chloride to ensure complete precipitation. Wash by decantation the precipitate with boiling distilled water. Transfer the precipitate to the filter paper and again wash with hot water till free from barium ions (test with dilute sulphuric acid) and also from chloride ions (test with silver nitrate solution).

Dry the precipitate and separate it from the filter paper. Ignite the filter paper to an ash which is treated with a drop of concentrated hydrochloric acid and a drop of dilute sulphuric acid as before (see above). Transfer the precipitate to the crucible and heat to a constant weight.

$$\underset{233.42}{BaSO_4} \equiv \underset{96.06}{SO_4''} \equiv \underset{174.25}{K_2SO_4} \equiv \underset{249.7}{CuSO_4.5H_2O}$$
$$\equiv 2 \cdot FeSO_4.(NH_4)_2SO_4.6H_2O.$$
$$\tfrac{1}{2}(392.13) = 196.07$$

Weight of barium sulphate $\times$ 0.4115 = weight of SO_4''.

7. Estimation of Zinc Oxide in a Solution of Zinc Chloride or Zinc Sulphate.

Reaction—When sodium carbonate solution is added to a soluble zinc salt, carbonate is precipitated. This ignition gives zinc oxide:

$$ZnSO_4 + Na_2CO_3 = ZnCO_3 + Na_2SO_4.$$
$$ZnCO_3 = ZnO + CO_2.$$

Solution—The solution supplied has been prepared by dissolving a good sample of metallic zinc (18 g. per litre), or zinc oxide (25 g. per litre), or zinc sulphate crystals, $ZnSO_4.7H_2O$ (100 g.

per litre) in dilute sulphuric acid (some times in dilute hydrochloric acid even), 10 ml. of any of these solutions will give about 0·25 g. of the precipitate.

Process—If the metal or zinc oxide has been dissolved in acid, the solution is highly acidic. Boil the given solution after adding 20 ml. of water. To the hot solution, add hot sodium carbonate solution. When a permanent precipitate has been obtained, add a drop of phenolphthalein solution. Add a further quantity of hot sodium carbonate solution to the hot zinc solution till a very faint pink coloration is obtained (just as in acid—alkali titrations). If the colour is too much pink, neutralise the alkali with a very dilute hydrochloric acid, till the solution remains just faintly pinkish even in the boiling state. Allow the precipitate to settle, and then begin filtration. Wash it several times by decantation with hot water, till free from sulphate ions (if the original solution was sulphate; otherwise from chloride ions if the solution was of a chloride). Transfer the precipitate to the filter paper and dry on a chimney.

Separate the precipitate on a clock glass and again place the filter paper in the funnel, and soak it with strong solution of ammonium nitrate (5 g. in 5 ml. of water). Again dry the filter paper on the chimney. Ignite the filter paper and collect the ash in the crucible as usual. Heat the ash till it is clear (if the paper remains unburnt, cool the crucible and add a crystal of ammonium nitrate and again heat). Now cool the crucible, and transfer the precipitate and heat it to a constant weight.

$$\underset{65.38}{Zn} \equiv \underset{81.38}{ZnO} \equiv \underset{287\cdot44}{ZnSO_4.7H_2O}.$$

Weight of $ZnO \times 0\cdot8034 =$ Weight of Zn.

Treatment of the ash—Zinc oxide is likely to be reduced by the carbon of the filter paper to metallic zinc. The metal is volatile at the temperature of the Bunsen flame and hence it would mean a loss. For this reason, the filter paper is soaked with ammonium nitrate before ignition. The ammonium salt oxidises zinc to zinc oxide as soon as it is formed, and thus prevents the loss.

$$ZnCO_3 + 2C = Zn + 3CO \ ; \ ZnO + C = Zn + CO.$$
$$Zn + 2NH_4NO_3 = ZnO + N_2O + 4H_2O.$$

8. Estimation of Aluminium as Oxide in a Solution of Potash Alum.

Reaction—Aluminium is precipitated as hydroxide by adding ammonium hydroxide to an aluminium salt solution in presence

of ammonium chloride, the hydroxide is then converted into oxide, Al_2O_3 by ignition and weighed as such.

$$Al_2(SO_4)_3+6NH_4OH=2Al(OH)_3+3(NH_4)_2SO_4.$$
$$2Al\ (OH)_3=Al_2O_3+3H_2O.$$

Potash alum is a double salt, potassium aluminium sulphate $K_2SO_4.Al_2(SO_4)_3\ 24H_2O$. Potassium sulphate does not interfere in the reaction.

Solution—The solution supplied has been prepared by weighing a pure sample of potash alum, and dissolving in water. If the estimation has to be done in a 10 ml. solution, one ought to weigh about 140 g. of potash alum for a litre solution (or 2·4 g. for each estimation); this would give about 0·25 g. of Al_2O_3.

Process—Add about 50 ml. of water to the given solution and about 20 ml. of ammonium chloride from the shelf reagent (10% solution). Heat the solution to boiling, and then add ammonium hydroxide solution, till ammonia is just in excess; this is assured by stirring the solution and perceiving a distinct odour of ammonia. Add a small pinch of tannic acid (to coagulate the precipitate and facilitate filtration), and allow the precipitate to stand for some time. Boil the contents carefully till there is left only a faint odour of ammonia.

Allow the precipitate to settle. Filter the precipitate (wash the precipitate as far as possible by decantation), wash it with boiling water, or preferably with a 2% solution of ammonium nitrate until it is free from sulphate ions (test it with barium chloride solution in the filtrate). Dry the precipitate, and transfer it into the crucible along with the filter paper ash and ignite it to Al_2O_3 till a constant weight is obtained.

$$\begin{array}{llll} 2Al & \equiv\ Al_2(SO_4)_3 & \equiv\ K_2SO_4.Al_2(SO_4)_3 24H_2O & \equiv Al_2O_3. \\ 26.97\times2 & \quad 342.48 & \qquad\qquad 948.85 & \ 101.94 \\ =53{\cdot}94 & & & \end{array}$$

Weight of $Al_2O_3\times0{\cdot}5291$=Weight of Al.

Note—Alumina is not easily reduced by the carbon of the filter paper and hence the paper and the precipitate can be ignited together.

9. Estimation of Calcium as Oxide in a Sample of Calcium Carbonate (or a Solution of Calcium Chloride).

Reaction—Calcium is precipitated from the solution as calcium oxalate by the addition of ammonium oxalate in presence of ammonia; the oxalate is then ignited strongly to CaO.

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 \downarrow + 2NH_4Cl.$$
$$CaC_2O_4 = CaCO_3 + CO = CaO + CO_2 + CO.$$

Solution—Pure calcium carbonate is weighed and dissolved in hydrochloric acid. Iceland spar is the reliable sample. For each estimation one ought to weigh 0·4 to 0·5 g. of pure calcium carbonate to get 0·25 g. of CaO (40·50 g. of the carbonate for a litre of the solution if 10 ml. used for each estimation).

Process—Add about 20 ml. of water to the given solution and heat the solution to boiling. Then add a slight excess of ammonium hydroxide solution, boil and finally add a boiling solution of ammonium oxalate slowly till it is in moderate excess.

Allow the solution to stand for some time till the precipitate settles down. Then pour off the liquid through a gravimetric filter paper, taking care not to disturb the precipitate the least. Wash the precipitate in the beaker three to four times by decantation with hot water (preferably containing a little ammonium oxalate). Transfer the precipitate to the filter paper, and wash it with hot water till free from chloride (test with silver nitrate and dilute nitric acid added *in excess*). Dry the precipitate over a chimney. Transfer it to the crucible along with the ash and ignite it strongly to white heat (use a blow pipe) till the weight is constant. (First ignite over the Bunsen flame, and then on a blow pipe),

$$\underset{40.08}{Ca} \equiv \underset{56.08}{CaO} \equiv \underset{100\ 09}{CaCO_3} \equiv \underset{128.10}{CaC_2O_4}.$$

The weight of $CaO \times 0·147 =$ The weight of Ca.

N.B.—A quick final weighing is necessary as CaO is hygroscopic.

10. Estimation of Lead as Lead Sulphate in a Solution of Lead Nitrate.

Reaction—On the addition of dilute sulphuric acid, lead nitrate gives a precipitate of lead sulphate. The precipitation is complete only when alcohol is added :

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 \downarrow + 2HNO_3 .$$

Solution—Weigh out accurately about 0·3 g. of pure lead nitrate and dissolve the crystals in the least possible quantity of water. In case the solution is turbid, add a few drops of acetic acid.

Process—To the cold solution to be estimated, add dilute sulphuric acid in excess, and allow the precipitate to settle. Again add a few drops of the dilute acid to the supernatant liquid.

Finally complete the precipitation by the addition of 50 ml. of methylated (or rectified) spirit. Stir the solution and filter. Wash the precipitate with water acidified with sulphuric acid (1 part of acid in 10 parts of water), and finally with spirit till free from sulphate.

Dry the precipitate over a chimney. Remove the precipitate to a dry dish or collect it on the glazed paper and cover it with a dry funnel. Burn the filter paper and collect the ash in the crucible. During the process of incineration, a portion of the precipitate is reduced to lead sulphide. Reconvert it to lead sulphate by adding one drop of concentrated nitric acid and one drop of concentrated sulphuric acid to the ash (add the acids after cooling the crucible). Heat the crucible and when free from fumes, cool it and transfer the main precipitate to it. Heat the crucible to a dull red-heat, cool and weigh. Heat it again to a constant weight.

$$\underset{331.23}{Pb(NO_3)_2} = \underset{303 \cdot 27}{PbSO_4} = \underset{207 \cdot 21}{Pb.}$$

Weight of lead sulphate $\times 0 \cdot 6833 =$ weight of Pb.

Estimation of lead as lead chromate—Weigh out accurately about $0 \cdot 3$ g. of lead nitrate and dissolve in 200 ml. of water and add acetic acid to the solution till it is distinctly acidic. Heat and to the hot solution, add 4 per cent potassium dichromate solution in slight excess. Continue heating until the colour of the precipitate is definitely yellow. The supernatant liquid should possess yellow colour. Allow the precipitate to settle, filter it through a Gooch crucible, wash it with hot water and finally once with dilute alcohol. Heat the crucible in an air oven to a constant weight.

The lead chromate is somewhat of an indefinite composition.
Weight of Pb $CrO_4 \times 0 \cdot 6375 =$ Weight of Pb.

The theoretical factor is $0 \cdot 6411$, but the arbitrary one gives more concordant values.

11. Estimation of Chromium as Chromic Oxide in a Solution of Potassium Dichromate.

Reaction—Dichromate is reduced to a chromium salt by alcohol in presence of dilute sulphuric acid.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5OH = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3CH_3CHO.$$

The chromium salt with ammonium hydroxide gives a precipitate of chromic hydroxide, which when ignited gives c **romic** oxide:

$$Cr_2(SO_4)_3+6NH_4OH=2Cr(OH)_3\downarrow+3(NH_4)_2SO_4.$$
$$2Cr(OH)_3=Cr_2O_3+3H_2O.$$

Solution—Weigh about 0·3 g. of potassium dichromate for each estimation. A stock solution of 30 g. of the salt per litre may be prepared of which 10 ml. be taken for estimations.

Process—Acidify the given solution with 5 ml. of dilute sulphuric acid, and add 2 ml. of ethyl alcohol. A green solution will be obtained. Add 40 ml. of water and heat till free from aldehyde vapours. To the hot solution, add ammonium hydroxide solution just in excess. Allow the precipitate to settle. Filter out the precipitate, wash it with hot water by decantation and then transfer the precipitate to the filter paper. Finally, wash it free from sulphate. Dry the precipitate over a chimney, transfer it to the crucible and ignite as usua (add a drop of strong nitric acid to the ash).

$$K_2Cr_2O_7\equiv Cr_2O_3\equiv 2Cr.$$
$$294\cdot21 \qquad 152\cdot02 \qquad 2\times52\cdot01=104\cdot02.$$
$$\text{Weight of } Cr_2O_3\times0.6841=\text{Weight of } Cr.$$

12. Estimation of Magnesium as Magnesium Pyrophosphate in a Solution of Magnesium Sulphate

Reaction—Magnesium precipitated as magnesium ammonium phosphate by the addition of microcosmic salt (sodium ammonium hydrogen phosphate, $NaNH_4HPO_4.4H_2O$ prepared by dissolving 6 g. of ammonium chloride and 36 g. of sodium phosphate, Na_2HPO_4, in a little hot water and crystallising) or simply by sodium phosphate. The precipitate is ignited to form magnesium pyrophosphate:

$$MgSO_4+NaNH_4HPO_4=MgNH_4PO_4\downarrow+NaHSO_4.$$
$$2Mg.NH_4PO_4=Mg_2P_2O_7+2NH_3+H_2O.$$

Solution—0·05 g. of magnesium ribbon dissolved in dilute sulphuric acid would yield a solution, which would give about 0·25 g. of $Mg_2P_2O_7$. If the crystallised magnesium sulphate, $MgSO_4.7H_2O$, is taken, it ought to be weighed about 0·6 g. to give about 0·25 g. of the pyrophosphate. For a litre solution, thus, take 5 g. of magnesium wire or 60 g. of magnesium sulphate crystals and estimate in 10 ml. of the solution.

Process—To the given solution, add about 10 ml. of water and 10 ml. of ammonium chloride solution from the shelf. Now add ammonium hydroxide, till the solution distinctly smells of ammonia. In case the solution is turbid, add more ammonium chloride till it is clear. To this, now add microcosmic salt solution (or even sodium hydrogen phosphate) with constant stirring.

Allow the precipitate to settle for some time. Test the supernatant clear liquid with a few drops of sodium hydrogen phosphate to ensure complete precipitation. Allow the precipitate now to stand over night. Wash the precipitate by decantation several times with water containing ammonia. Transfer the precipitate and again wash with ammonium hydroxide solution (shelf reagent diluted two times). Wash the precipitate till free from chloride (test with silver nitrate solution in presence of dilute nitric acid). Dry the precipitate as usual, and transfer it to the crucible. Ignite the precipitate and ash together to a constant weight.

$$\begin{array}{cccc} 2Mg \equiv & 2MgO \equiv & Mg_2P_2O_7 \equiv & 2MgSO_4.7H_2O \\ 24.32\times 2 & 40.32\times 2 & 222.68 & 2\times 246.42 \\ =48.64 & =80.64 & & =492\cdot 84 \end{array}$$

Weight of $Mg_2P_2O_7 \times 0.2184$ = Weight of Mg.

13. Estimation of Nickel as Nickel-dimethyl-glyoxime Complex in a Solution of a Nickel Salt.

Reaction—Nickel salts form a chelate complex with dimethyl-glyoxime, $[CH_3.C:NOH]_2$.

$$NiSO_4+2(CH_3.C:NOH)_2=Ni\ (CH_3.C:NOH.NO:C.CH_3)_2.+H_2SO_4$$

Solution—Weight out accurately 0·3-0·4 g. of pure nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$; dissolve it in 200 ml. of water, and add 5 ml. of dilute hydrochloric acid (1 : 1). Use the whole of it for estimation.

Process—Warm the solution of the nickel salt to 80°, and add a slight excess of dimethylglyoxime reagent and immediately add dilute ammonia solution drop by drop and with constant stirring until precipitation takes place, and then in slight excess. Allow the precipitate to stand on steam bath for half an hour, and when the red precipitate has settled out test for complete precipitation. Allow the precipitate to stand further for one hour, and cool it simultaneously. Filter the cold solution through a Gooch or sintered glass crucible. Wash the precipitate with cold water, till free from chloride; and dry it at 100-120° for one hour, cool in the desiccator and weigh.

$$\begin{array}{cc} Ni\ (C_4H_2O_2N_2)_2 \equiv & Ni \\ 288.69 & 58.69 \end{array}$$

Weight of Ni chelate $\times 0.2033$ = weight of Ni.

Analysis of a Silver Coin.

An old type of silver coin used to contain about 90% silver and 10% copper. The coin is cut into pieces and a known weight of it is dissolved in concentrated nitric acid (half-diluted).

(i) Silver is precipitated as chloride by dilute hydrochloric acid (*see silver estimation*), filtered and the filtrate kept for copper estimation. The precipitate is dried, and weighed as AgCl.

(ii) The filtrate is boiled and treated with hot caustic soda solution, the precipitated copper oxide is filtered, washed, ignited and weighed as CuO (*see the estimation of copper*).

Solution of alloy—Take a four anna silver coin and thin it by hammering. Clean the surface with a sand paper, and cut it into small pieces. Weight out about 0. 5 g. of the coin accurately and place it in a porcelain basin. Add about 5 ml. of strong nitric acid (half-diluted), and warm carefully. Add more of the acid if the coin does not dissolve completely. To eliminate the loss by spurting, cover the dish carefully with an inverted funnel). When the solution is complete, remove the funnel, and wash its inner surface, collecting the washings in a beaker. Now place the dish on a water bath and evaporate the contents to dryness, and thus free it from the extra nitric acid fumes. Dissolve the residue in about 30 ml. of water and mix the solution with the funnel washings.

The solution is ready. Now add dilute hydrochloric acid to precipitate silver as chloride, and proceed as described above.

Calculate the amount of silver and copper per 100 g. of the coin from the weights of AgCl and CuO.

Analysis of Haematite free from Sulphur and Phosphates.

The Indian haematite has approximately the following composition: Iron 64, silica 2.1, lime 0.5, alumina 1.25 and magnesia 0.18 per cent. Besides, it contains traces of manganese, sulphur and phosphates. A student at this stage requires the estimation of silica, alumina, magnesia and iron in a given sample, besides the estimation of moisture.

Estimation of moisture—Take a sample of haematite and powder it as fine as possible. Weigh about 2 g. of the sample accurately between two watch glasses loosely fitting over each other and placed between a clip. Place the substance in an air oven maintained at 120° after taking out upper watch glass and the clip. Replace the upper watch glass and weigh after a couple of hours. Again heat the contents in the same way and determine the weight. Repeat the process till the weight is constant. The difference between the initial and final weighings will give the moisture content.

Weight of haematite powder $= m_1$.
Weight of watch glasses with ore $= m_2$.
The constant weight on heating $= m_3$.

$$\text{Precentage of moisture} = (m_2 - m_3)\frac{100}{m_1}.$$

Estimation of silica—Weigh accurately 5—12 g. of the finely powdered ore, transfer it to a porcelain dish (80 ml. capacity), and heat it on a wire gauze with concentrated hydrochloric acid (20 ml.) and a little strong nitric acid. Continue heating till all soluble matter has dissolved (at this stage the residue undissolved will turn white from brown). Transfer the dish to a water bath and evaporate the contents to dryness, and now heat the residue to 110° in an oven. Make sure that all the nitric acid has been driven off.

Treat the dry reside thus obtained with concentrated hydrochloric acid. Then dilute the solution and heat it. Deacant off the clear liquid through a filter paper. Treat the residue again with a small quantity of hydrochloric acid, and filter the solution through the same filter paper and collect it along with the same filtrate. The digestion with hydrochloric acid is continued till iron is extracted out completely, (test in the last drop of the filtrate with a drop of potassium ferrocyanide). Wash and transfer the residue to the filter paper, dry and ignite it in a weighed crucible. Weigh now the crucible; the difference of the two readings will give the amount of silica. Calculate the percentage as above.

Estimation of iron and aluminium jointly—(If manganese absent)—Dilute the filtrate and washings from silica, and raise the solution to 250 ml. mark in a graduated flask. Take 100 ml. of the solution by means of a pipette, and add 15 ml. of ammonium chloride solution; boil the solution and add ammonium hydroxide in excess (add tannic acid to coagulate aluminium if necessary). Allow the mixed precipitates of iron and aluminium hydroxides to settle. Now wash the precipitate by decantation with hot water through a filter paper. The filtrates and washings are kept preserved for calcium and magnesium estimations.

The mixed precipitates of oxides may be again dissolved by adding hydrochloric acid on the filter paper and collecting the filtrate in a beaker; the filter paper is very well washed with hydrochloric acid and iron and aluminium hydroxide reprecipitated by adding ammonium hydroxide to their hot solution. The precipitate is washed, transferred to the filter paper, dried and finally ignited to a constant weight.

This gives the mixed values of Al_2O_3 and Fe_2O_3 for 100 ml. of the solution. From this, calculate for the total bulk of the solution.

Estimation of iron volumetrically—Take 25 ml. of the original solution from the graduated flask, and dilute it to 250 ml. in another flask. Take 25 ml. of this diluted solution, and reduce it with stannous chloride solution taken in excess. Remove the excess of stannous chloride by adding a solution of mercuric chloride (the calomel is precipitated). The white precipitate that appears

will not interfere with titration. Now titrate the ferrous iron with $N/20$ potassium dichromate solution. From the titration readings, calculate the value corresponding to Fe_2O_3.

Subtract this weight of Fe_2O_3 from the mixed weights determined gravimetrically. That will give Al_2O_3.

Estimation of calcium—Take the washings and filtrates from the mixed oxides of iron and aluminium. Heat the solution and add powdered ammonium oxalate in slight excess; the precipitate of calcium oxalate will be obtained. Boil the solution and allow the precipitate to settle. To the supernatant liquid, add a few drops of ammonium oxalate solution more to ensure complete precipitation. Boil and filter the precipitate; wash it with hot water till free from chloride. Dry the precipitate, and ignite it first on the Bunsen flame and finally on a blow pipe, and weigh it as CaO.

Do not throw off the filtrate from the precipitated calcium oxalate. It is used for the estimation of magnesium.

Estimation of magnesium—Take the filtrate from calcium oxalate in porcelain dish; evaporate it on water bath to a small bulk and finally carefully on a sand bath to dryness—stir it constantly with a glass rod during the last stages so that it does not spurt. Heating on the sand bath thus removes all the ammonium chloride which gives white fumes. Dissolve the residue in strong hydrochloric acid (filter if necessary), and treat it with an excess of ammonium hydroxide and then sodium hydrogen phosphate. Allow the precipitate to stand over-night and filter the next day. Wash the precipitate with ammonium hydroxide solution till free from chloride. Dry the precipitate, ignite and weigh as $Mg_2P_2O_7$. From this weighing, calculate the amount corresponding to MgO, and find out the percentage in the original ore.

Record your results of analysis in the following way:

Constituent	Amounts of ore taken $= m$ g. Amt. in '*m*' gram of the ore.	Percentage
Moisture	...	...
Silica	...	...
Fe_2O_3	...	...
Al_2O_3	...	...
CaO	...	...
MgO	...	...

PART VI

Volumetric Analysis

The volumetric reactions which we shall be considering in the present chapter fall into three main groups:

(*a*) Acid-alkali titrations, (*b*) oxidation-reduction reactions, and (*c*) precipitation reactions.

The success of a volumeteric analysis depends upon the use of accurately calibrated apparatus, *e.g.*, burette, pipette and measuring flasks, and upon the accuracy of weighings by means of a chemical balance.

Standard solutions—The most important point in volumetric analysis is the preparation of standard solution. A standard solution is a solution of definite concentration, the strength of which depends upon the problem undertaken. The strength of solutions is generally expressed in terms of normality.

A normal solution of a substance is the solution, one litre of which contains the equivalent weight of that substance in grams. This is written as N. Similarly, 3 N, $N/5$, (or $0{\cdot}2N$) and $N/20$ (or $0.05N$) are the solutions containing thrice, one-fifth and one-twentieth respectively of the gram-equivalent weight of the substance per litre.

Gram-Equivalent Weight—Gram-equivalent weight of a substance is that weight in grams which is chemically equivalent to 1. 008 g. of hydrogen, 8 g. of oxygen or 35.46 g. of chlorine.

(*i*) *Acid-Alkali titrations*—These reactions are between H^+ and OH^- ions: $H^+ + OH^- = H_2O$. In order to determine equivalent weight of *an acid*, we must know how many replaceable hydrogen atoms it contains. If there is only one replaceable hydrogen atom, the molecular weight (mol. wt.) will itselfbe the equivalent weight; if there are 2 replaceable hydrogen atoms, equivalent weight will be $\frac{\text{mol. wt.}}{2}$. Thus we have

$$\text{Eq. wt. of HCl} = \frac{36.45}{1} = 36.46.$$

$$\text{Eq. wt. of } H_2SO_4 = \frac{93}{2} = 49.$$

$$\text{Eq. wt. of } HNO_3 = \frac{63}{1} = 63.$$

$$\text{Eq. wt. of } H_2C_2O_4.2H_2O = \frac{126}{2} = 63.$$

Similarly, the eq. wt. of an alkali is determined by knowing the number of replaceable OH groups. Thus.

$$\text{Eq. wt. of } NaOH = \frac{40}{1} = 40$$

$$\text{Eq. wt. of } KOH = \frac{56.1}{1} = 56.1$$

$$\text{Eq. wt. of } Na_2CO_3 \,(\equiv 2NaOH) = \frac{106}{2} = 53.$$

From the idea of equivalents given above, it becomes clear that a certain volume of a NORMAL solution of caustic soda will neutralise the same volume of a NORMAL solution of any acid.

(*ii*) *Oxidation-reduction reaction.*—In such reactions, the gram-equivalent weight of a compound is that weight of the compound which can oxidise 1.008 g. of hydrogen or supply 8 g. of oxygen for oxidation. Thus $K_2Cr_2O_7$ in acid solution can supply oxygen according to the equation:

$$K_2Cr_2O_7 \rightarrow K_2O + Cr_2O_3 + 3O;$$

its one molecule can supply three atoms of oxygen for oxidation. Thus:

$$K_2Cr_2O_7 \equiv 3O \equiv 6H$$

$$\text{Eq. wt. of } K_2Cr_2O_7 = \frac{294.21}{6} = 49.03.$$

Potassium permanganate in presence of dilute sulphuric acid can supply oxygen as:

$$2KMnO_4 \rightarrow K_2O + 2MnO + 5O.$$

Thus two molecules of $KMnO_4$ supply 5 atoms of oxygen for oxidation.

$$2KMnO_4 \equiv 5O \equiv 10H$$

$$\text{Eq. wt.} = \frac{2KMnO_4}{10} = \frac{316 \cdot 06}{10} = 31.606.$$

It is important to remember that the equivalent weight of a substance does not remain the same under all conditions. Thus $KMnO_4$ in an alkaline solution gives only 3 atoms of oxygen per

its two molecules for oxidation (unlike 5 atoms of oxygen in acidic solution) as:—

$$2KMnO_4 \rightarrow K_2O + 2MnO_2 + 3O.$$

Therefore, $2KMnO_4 \equiv 3O \equiv 6H$.

$$\text{Eq. wt.} = \frac{2KMnO_4}{6} = \frac{316.06}{6} = 52\cdot68.$$

Ferrous sulphate in presence of an acid is oxidised to ferric sulphate by potassium dichromate and permanganate as:

(*i*) $K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$

$6FeSO_4 + 3H_2SO_4 + 3O \rightarrow 3Fe_2(SO_4)_3 + 3H_2O.$

$$K_2Cr_2O_7 \equiv 6FeSO_4.$$

(*ii*) $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$

$10\ FeSO_4 + 5H_2SO_4 + 5O \rightarrow 5Fe_2(SO_4)_3 + 5H_2O.$

$$2KMnO_4 \equiv 5O \equiv 10H \equiv 10\ FeSO_4.$$

In the former case, one mol. of $K_2Cr_2O_7$ oxidises 6 mols. of ferrous sulphate (or similarly ferrous ammonium sulphate (and as the eq. wt. of $K_2Cr_2O_7$ is one-sixth of its molecular weight, the eq. wt. of ferrous ammonium sulphate will be the same as its mol. wt. The same result is obtained by considering the second reaction. Ten mols of ferrous ammonium sulphate are oxidised by two mols of potassium permanganate. As the eq. wt. of permanganate is one-fifth of its mol. wt., the eq. wt. of ferrous ammonium sulphate will be the same as its molecular weight. Eq. wt. of ferrous ammonium sulphate

$$= \frac{FeSO_4.(NH_4)_2SO_4.6H_2O}{1} = \frac{392\cdot1}{1} = 392.1.$$

In *iodometry* the reaction between iodine and sodium thiosulphate is:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$
$$Na_2S_2O_3 \equiv I \equiv H.$$

Here 2 mols. of sodium thiosulphate are oxidised by two atoms of iodine, so that one mol. can be oxidised by one atom of iodine. Also as one atom of iodine can oxidise one atom of hydrogen, the equivalent weight of iodine will be 126.92 and that of sodium thiosulphate will be the same as its molecular weight.

126·52

Eq. wt. of iodine$=\frac{126\cdot92}{1}$ ~~1=26.92~~

$$\text{Eq. wt. of sodium thiosulphate} = \frac{Na_2S_2O_3.5H_2O}{1} = 248.21$$

When iodine is titrated against arsenious oxide, As_2O_3, iodine oxidises As_2O_3 to As_2O_5 as :

$$As_2O_3+2I_2+2H_2O=As_2O_5+4HI.$$
$$As_2O_3\equiv 4I\equiv 4H.$$

Here four atoms of iodine oxidise one molecule of arsenious oxide and as one atom of iodine is equivalent to one atom of hydrogen, the equivalent weight of arsenious oxide will be one-fourth of its molecular weight.

$$\text{Eq. wt. of } As_2O_3=\frac{As_2O_3}{4}=\frac{197.82}{4}=49.455.$$

When copper sulphate is used to liberate iodine from a solution of potassium iodide, the following reactions take place :

$$2CuSO_4+4KI=Cu_2I_2+2K_2SO_4+I_2.$$
$$CuSO_4\equiv I\equiv H.$$

Two molecules of copper sulphate liberate two atoms of iodine and as one atom of iodine is equivalent to one atom of hydrogen, the eq. wt. of copper sulphate will be the same as its molecular weight.

$$\text{Eq. wt. of copper sulphate}=\frac{CuSO_4.5H_2O}{1}=\frac{249.71}{1}$$
$$=249.71.$$

(*iii*) *Precipitation reactions*—In titrating silver nitrate against any chloride or potassium thiocyanate, KCNS, we have

$$AgNO_3+KCl=AgCl\downarrow+KNO_3.$$
$$AgNO_3+KCNS=AgCNS\downarrow+KNO_3.$$
$$AgNO_3\equiv KCl\equiv KCNS.$$

It is thus clear that one molecule of silver nitrate is equivalent to one molecule of potassium chloride or one molecule of potassium thiocyanate. Hence the equivalent weights of these substances will be the same as their molecular weights.

$$\text{Eq. wt. of } AgNO_3=\frac{AgNO_3}{1}=\frac{167.9}{1}=167.9.$$

$$\text{Eq. wt. of NaCl}=\frac{NaCl}{1}=\frac{58.45}{1}=58.45.$$

$$\text{Eq. wt. KCl}=\frac{KCl}{1}=\frac{74.45}{1}=74.45.$$

$$\text{Eq. wt. of KCNS}=\frac{KCNS}{1}=\frac{97.1}{1}=97.1.$$

A table of equivalent weights of common substances is given at the end of the book. These amounts in grams dissolved in a litre give normal solutions.

Use of Indicators—The most important point in volumetric analysis is the determination of the end point of a reaction. For this, we use certain substances, which change colour at the end point and by this change they indicate that the reaction is complete. Such a substance is called an *indicator*.

The quantity of the indicator to be used depends upon many factors, but it is always advisable to use the smallest possible quantity of these indicators which may be sufficient to produce appreciable change of colour.

We have three kinds of titrations with respect to the use of indicators :

(*i*) *Internal indicator*—In such cases, a substance which changes colour is added to the reacting medium, *e.g.*, phenolphthalein or methyl orange in titration of acids and alkalis, starch in iodometry and potassium chromate or ferric alum in titrations of silver nitrate with potassium chloride or potassium thiocyanate.

(*ii*) *External indicator*—In these cases, the indicator is not added to the reacting substances but it is used externally, *e.g.*, potassium ferricyanide in the titration of potassium dichromate with ferrous ammonium sulphate.

(*iii*) *Self indicator*—In these titrations, no indicator is used because the end of reaction is indicated by the colour of one of the reacting substances itself, *e.g.*, titration of oxalic acid or ferrous ammonium sulphate with potassium permanganate. The end point is indicated by the appearance of pink colour.

Actual procedure—Fill up your burette with one of the solutions and take the reading. Take a known volume of another solution (say 10 ml.) in a clean beaker by means of a pipette and add indicator to it. In some cases, it is advisable to add the indicator at half-way of the reaction, or a little before the end point. Now run in the second solution from the burette drop by drop, with constant stirring till the indicator changes colour. Take the reading. Repeat the process till you get two concordant readings.

Calculations—As equal volumes of equinormal solutions contain equivalent amounts of different substances, it follows that volumes of different substances of different strengths for the same volume of of a substance of known strength will vary inversely as their strengths. Thus the product of volume and strength will be constant.

(Strength $\times$ volume) of one solution

$=$(Strength $\times$ volume) of another solution

i.e. $s_1 \times v_1 = s_2 \times v_2$.

Strength is given in terms of normality. The amount per litre can be calculated by substituting the equivalent weight of the substance for N,

$$\frac{N}{x} \times v_1 = \frac{N}{y} \times v_2.$$

The volumetric work generally consists of double titrations.

The intermediate solution is titrated against ones own prepared standard solution, and thus standardised. The unknown solution is then titrated against the standardised intermediate solution and the strength calculated. The correct notion of reciprocity would save labour of calculations. Thus if 10 ml. of $KMnO_4$ are required for 10 ml. of $\frac{N}{19.1}$ oxalic acid (your own prepared) and 11·2 ml. of $KMnO_4$ for 10 ml. of the unknown oxalic acid then the strength of the unknown oxalic acid is $= \frac{N}{19.1} \times \frac{11.2}{10}$.

Theory of indicators

There are four types of indicators : (i) Hydrogen ion indicators, used in acid-alkali titrations; (ii) adsorption indicators as starch in iodine titration, and fluorescein, in silver estimation; (iii) precipitation indicators, as potassium chromate in silver chloride titration; and (iv) oxidation-reduction indicators as diphenylamine in potassium dichromate-ferrous sulphate titrations.

(i) *Hydrogen ion indicators*—A number of synthetic as well as natural colouring matters are known which show a change of colour under the action of acids and alkalis. Litmus, methyl orange, phenolphthalein, nitrophenols and methyl red are well-known indicators of this group.

According to Ostwald's theory of indicators, these substances are weak acids or weak bases, one radical of which in the ionic state has colour different from that in the undissociated state. Phenolphthalein functions as a very weak acid; its salts formed by the action of alkalis are highly dissociated giving an intense pink colour. In acidic solutions, the dissociation of this weak acid indicator is all the more depressed, and it gives hardly a phenolphthalate ion.

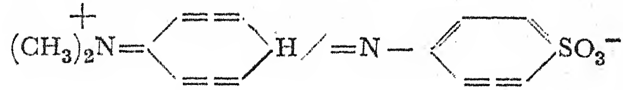
$HPh = H^+ + Ph^-$ (dissociation very small).

$NaOH \rightarrow$ (large dissociation).

$NaPh \rightarrow Na^+ + Ph^-$ (coloured).

Methyl orange is the sodium salt of a sulphonic acid and is largely ionised in solution. The anion,

is yellow. In presence of acids, this behaves as a weak base. H^+ ion gets attached to one of the N=N nitrogens, and rearranges to form a red ion with a quinonoid structure.



On the addition of alkalis, the structure again changes to that of the yellow ion.

On the modern theory of colours, phenolphthalein also gives a pink colour on account of its assuming a quinonoid structure. The quinonoid structure is destroyed in an acidic solution.

An ideal indicator is that which shows a change in colour at a pH 6.9. Phenolphthalein is colourless below a pH 8.3. Thus a solution just neutral to phenolphthalein is in fact slightly alkaline. A solution neutral to litmus is exactly neutral, the neutral point is at pH 6·9. A solution neutral to methyl orange is slightly acid (0.0005 N), methyl violet requires 0·01N acid for a colour change.

In acidimetry and alkalimetry, the choice of indicator depends upon the hydrogen ion concentration of the resulting salt. If a slightly alkaline salt, like sodium acetate or oxalate, is formed (alkaline due to the hydrolysis) at the neutral point, an indicator is used which will show a change in colour on the alkaline side. Such an indicator is phenolphthalein as we have already seen (the colour appears at pH 8.3), and it is, therefore, used in titrating a strong alkali like caustic soda with a weak acid like acetic or oxalic.

Common Indicators

Indicator	pH range	Colour	
		Acid	Alkaline
Bromocresol purple	5·2 to 6·8	Yellow	Purple
Bromophenol blue	3·0 to 4·6	Yellow	Bluish-violet
Bromothymol blue	6·0 to 7·6	Yellow	Blue
Cochineal	4·8 to 6·2	Yellow	Lilac pink
Congo red	3·0 to 5·0	Blue	Reddish-yellow
Litmus	4·5 to 8·3	Red	Blue
Methyl orange	3·1 to 4·4	Pink	Yellow
Methyl red	4·2 to 6·3	Red	Yellow
Phenol red	6·8 to 8.4	Yellow	Red
Phenolphthalein	8·0 to 9·8	Colourless	Red
Thymol blue	8·0 to 9·6	Yellow	Blue

If the resulting salt is slightly acidic at the neutral point, as is ammonium chloride, one has to choose an indicator which shows colour change on the acid side. In the case of methyl orange, the change in colour occurs between pH 4 and 6, and therefore, it is used in titrating weak base like ammonia solution with a strong acid like hyrochloric acid.

(ii) *Adsorption indicators*—Starch solution in water is a colloidal dispersion. The finely dispersed particles markedly adsorb free iodine, which presents a blue tint, when present in small concentrations. This fact is utilised in iodometric estimations, in which starch solution is used as an indicator. The solution of starch must be *fresh*.

A number of adsorption indicators are utilised in halide estimations. The precipitate of silver halide, when it is first formed from a solution is colloidal in nature and the particles are charged. The adsorption indicators are, for the most part, organic dyestuffs, as phenosafranine, fluorescein, etc., which can be adsorbed by the silver halides. On running a solution of sodium chloride into a solution of silver nitrate, the end point is clearly marked by the white precipitate of silver chloride becoming coloured.

(iii) *Precipitation indicators*—Potassium chromate is used as an indicator in the titration of silver nitrate with potassium chloride. This method of estimation of silver depends upon the fact that silver chromate, though comparatively insoluble is more soluble than silver chloride *and that the colour of silver chromate is red. The silver chromate dissolved will yield sufficient number of silver ions to exceed the solubility of silver chloride. Therefore, so long as chloride ions are present in a concentration sufficient to precipitate silver chloride, no silver chromate will come down as precipitate. The precipitate of silver chromate only appears when the concentration of chloride ions is so much reduced that the silver ions available from the solubility of silver chromate are sufficient to exceed the solubility of silver chloride.

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*The solubility products of the salts are not exactly comparable, as silver chromate per molecule gives three ions on dissociation, whereas silver chloride gives only two ions.

$$\text{For } AgCl\ [Ag^+]\ [Cl^-] = 1.2 \times 10^{-10}$$
$$\text{For } Ag_2CrO_4,\ [Ag^+]^2[CrO_4^{=}] = 1.7 \times 10^{-12}.$$

Thus, though the solubility of silver chromate is more than that of silver chloride its solubility product is less, as the square of silver ion concentration has been taken into account.

Silver chloride, 1.1×10^{-5} moles per litre soluble.

Silver chromate 7.5×10^{-5} moles per litre soluble.

In the titration of silver nitrate and potassium thiocyanate ferric alum is used as indicator. Silver thiocynate has a small, solubility : $8 \cdot 5 \times 10^{-7}$ moles per litre. Very few thiocyanate ions are available from this solubility. These ions are sufficient to produce undissociated molecules of ferric t iocyanate which alone exhibits the characteristic red colouration when present in sufficient concentration. When all silver ions have been precipitated out as silver thiocyanate, the addition of a further quantity of potassium thiocyanate gives a red colouration of ferric thiocyanate with ferric alum.

(iv) *Oxidation-reduction indicators*—The use of the indicator depends upon the relative redox (abbreviation of reduction-oxidation) potentials. The familiar example is the use of *sodium diphenylamine sulphonate* in ferrous-dichromate titrations. The chromate is an oxidising agent : It oxidises ferrous ions to ferric and also the diphenylamine salt to a bluish grey colour. But the redox potentials for the two reactions are such that so long as ferrous ions are present, they are preferentially oxidised and the oxidation of diphenylamine sulphonate only occurs after the disappearance of ferrous ions.

Sodium diphenyl amine sulphonate is prepared by stirring 0.32 g. of barium diphenylamine sulphonate in 90 ml. of water, and adding 0.5 g. sodium sulphate in 10 ml. of water. After the mixture has been stirred for some time, the precipitate is filtered off. Six to eight drops of the filtrate are used for each titration.

SECTION I

Acidimetry and Alkalimetry

In a neutral solution, the concentrations of hydrogen and hydroxyl ions are equal. In pure neutral water, $C_H = 10^{-7}$ and $C_{OH} = 10^{-7}$ gram-equivalents per litre. The pH of this solution is 7: when pH is less then 7, the solution is acidic: and when it is more than 7, it is alkaline; PH of $N/10$ NaOH solution is 13 and $N/10$ HCl is 1.

When an acid is being estimated by titration with a standard solution of an alkali, one does not necessarily aim at producing a neutral solution. One simply wants to find out a quantity of the base *equivalent* to that of the acid. It is only when the base and acid are *both strong*, the resulting solution is exactly neutral; in other cases, the hydrolysis of the resulting salt makes the solution alkaline or acidic :

$$CH_3COONa + H_2O \rightarrow CH_3COOH + Na^+ + OH^- \text{(alkaline)}.$$

Methyl orange is yellow in all solutions of pH greater than 4 (it is not affected by HCN, H_2CO_3 and boric acid which have pH always more than 4). The colour of this indicator changes from red to yellow between pH 2.9—4.0.

Phenolphthalein (used in alcoholic solution) is colourless. It gives a pink colour on the alkaline side; its range of use is 8.3-10.0; it is suitable for the titration of inorganic and organic acids with *strong bases* (as with NaOH); but it cannot be used in the presence of carbonic acid or of ammonium salts (not with Na_2CO_3 or NH_4OH). For accurate work the caustic alkali solution should be protected from carbon dioxide.

Standard Solutions—(i) *Standard solution of sodium carbonate*—A pure sample of *anhydrous* sodium carbonate is usually available. If not, heat sodium bicarbonate in a porcelain dish to redness till the weight is constant; and use the sample.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

For a normal solution, one requires 53 g. per litre.

(ii) *Standard oxalic acid solution*—A normal solution of oxalic acid would require 63.00 g. of the crystallised oxalic acid, $H_2C_2O_4.2H_2O$, per litre. There is no difficulty in weighing and preparing solution of this acid.

(iii) *Standard solution of sulphuric acid*—The solutions of sulphuric acid, at different concentrations, have different densities as given below (concentrations are given as percentages by weight of H_2SO_4 and at 15°) :

Sp. gr.	% H_2SO_4	Sp. gr.	% H_2SO_4
1.005	0.83	1.500	59·70
1.030	4.49	1.550	64·16
1.070	10.19	1.600	68·51
1.100	14.35	1.650	72·82
1.150	20.91	1.700	77·17
1·200	27·32	1·750	81·56
1.250	33·43	1·800	86·90
1.300	39·91	1·810	90·05
1.353	44·82	1·840	95·60
1.400	50·11	1·840	98·20
1.450	55·03	1·8385	99·95

A normal solution requires 49 grams of sulphuric acid per litre. But the pure sulphuric acid is rarely obtained, as it is always

mixed up with water, its standard solution cannot be prepared by weighing. From the above table, one can find out the density corresponding to the required concentration, and prepare the solution of this specific gravity. This approximate solution is titrated against an alkali solution of the known strength.

It is advisable to prepare an acid, stronger than the required, and then dilute it to the required strength after titration.

Suppose we are required to prepare 250 ml. of $N/10$ sulphuric acid, and the stock solution of sulphuric acid that we have prepared gives the strength on titration as $N/5.5$; now :

$$\frac{N}{5.5}\times x \text{ ml.}=\frac{1N}{10}\times 250 \text{ ml.}$$

$$x=\frac{1}{10}\times 250\times 5.5 \text{ ml.}$$

$$=137.5 \text{ ml.}$$

Therefore, if we take by burette and pipette, 137.5 ml. of $N/5.5$ sulphuric acid in a 250 ml. flask and dilute it to the standard mark, the acid thus diluted will have the strength $N/10$. One can always prepare a standard solution of an acid, by diluting a *stronger* acid of a known strength.

Sulphuric acid is titrated against standard sodium carbonate solution, using methyl orange as indicator. Acid solution is taken in the burette, and 10 ml. (or 20 ml.) of the standard sodium carbonate solution are pipetted out in a clean beaker (the pipette is always rinsed before use with the solution to be pipetted). The beaker is placed on a white paper or tile, and the acid run from the burette till the colour just changes from yellow to pink.

(iv) *Standard solution of caustic soda*—A normal solution contains 40.00 g. of NaOH per litre. It is prepared by dissolving the caustic soda sticks (weighed approximately) in water free from carbon dioxide (*i.e.*, in water which has been boiled); it is then standardised by titration against a standard acid solution (say caustic soda, using phenolphthalein as indicator).

If one intends preparing a solution of an exact specified strength, he ought to prepare a solution of higher concentration, and then dilute it according to calculations.

Suppose the stock solution standardised is of $N/15.20$ strength and one requires to have 200 ml. of $N/20$ NaOH from it.

$$\frac{N}{15.2}\times x \text{ ml.}=\frac{N}{20}\times 200 \text{ ml.}$$

$$x=\frac{1}{20}\times 200\times 15{\cdot}20=152$$

Thus 152.0 ml. of $\frac{N}{15.20}$ NaOH when pipetted out in a 200 ml. flask, and raised to the standard mark will give an alkali of $N/20$ strength:

(v) *Standard solution of hydrochloric acid*—It is prepared in the same way as sulphuric acid, and titrated against a standard solution of sodium carbonate (methyl orange as indicator), or against a solution of caustic soda (phenolphthalein as indicator).

(vi) *Standard solution of borax*—Borax, $Na_2B_4O_7 . 10H_2O$ (sodium tetraborate decahydrate) is a very convenient alkali for standardisations. It can be easily purified by recrystallisation: it has a large equivalent weight, 190.72, and a sharp end point can be obtained with methyl red at room temperatures, since this indicator has no effect upon the very weak boric acid. Reaction in titration is:

$$Na_2B_4O_7.10H_2O+2HCl=2NaCl+4H_3BO_3+5H_2O.$$

Crystallisation of borax—Dissolve 15 g. of borax in 50 ml. of water and crystallise at the room temperature. Filter the crystals at the pump, wash twice with water and then twice with portions of 95 per cent alcohol, and finally twice with ether. Spread borax in thin layers on a clock glass to dry at the room temperature.

For elementary work, one can weigh out 4·7—4·8 g. of A.R. borax on a watch glass or in a small beaker for a 250 ml. volume.

(vii) *Mercuric oxide solution*—Mercuric oxide dissolves in potassium bromide solution with the production of potassium mercuric bromide and an equivalent quantity of potassium hydroxide:

$$HgO+4KBr+H_2O=K_2(HgBr_4)+2KOH.$$

A $0{\cdot}1N$ solution of KOH is thus obtained by dissolving 10·83 g. of A.R. mercuric oxide in a solution of 200 g. of A. R. potassium bromide in 300 ml. of water, and then raising to 1 litre. This solution can be used for titrating acids, using phenolphthalein or methyl orange as indicator.

(vii) *Standard baryta solution*—Barium hydroxide or baryta solution is widely used for titrating organic acids. Since barium carbonate is insoluble, baryta solution is a carbonate-free strong alkali. Its standard solution cannot be, however, prepared by direct weighing. To prepare an approximately $0.1N$ solution, dissolve 18 g. of A.R. crystallised baryta, $Ba(OH)_2.8H_2O$, or 20 g. of the commercial substance in 1 litre of volume. Decant the solution after having allowed it to stand for 2 days. A soda-lime guard tube is provided to prevent ingress of carbon dioxide. The solution must be standardised against $0.1N$ hydrochloric acid using phenolphthalein or thymol blue as indicator.

No. 1

Estimation of caustic soda and sodium carbonate in a mixture of both.

Take 20 ml. of the given solution in a beaker, and a standard solution of sulphuric acid (say $N/10$) in the burette. Use phenolphthalein as indicator and titrate.

$$2NaOH+H_2SO_4=Na_2SO_4+H_2O.$$

$$2Na_2CO_3+H_2SO_4=2NaHCO_3+Na_2SO_4.$$

Caustic soda gives the complete titre value. While sodium carbonate gives pink colour with phenolphthalein, sodium bicarbonate does not, and therefore, the end point is approached the moment, the whole carbonate is changed to bicarbonate.

At this stage, add a few drops of methyl orange (which would give a yellow colour), and titrate further with the standard solution of sulphuric acid, till the red colour is just obtained.

$$2NaHCO_3+H_2SO_4=Na_2SO_4+2H_2O+CO_2.$$

Sodium bicarbonate acts on methyl orange, whereas sodium sulphate does not. Repeat the readings.

Example—20 ml. of the solution taken and titrated with $N/10$ sulphuric acid:

1. When phenolphthalein was added, the end point appeared at 20 ml. of the acid.

2. After this, methyl orange added; the further acid required=2.5 ml.

$\therefore NaHCO_3 \rightarrow Na_2SO_4$ requires 2.5 ml. of $N/10$ H_2SO_4.

$\therefore Na_2CO_3 \rightarrow Na_2SO_4$ requires $2.5\times 2=5.0$ ml. of $N/10$ H_2SO_4.

Out of the total (20+2.5) or 22.5 ml. of the acid, 5.0 ml. correspond to Na_2CO_3, and the rest 22.5—5.0=17.5 ml. correspond to NaOH.

Numerical—A mixed solution of potassium hydroxide and sodium carbonate required 20 ml. of $N/20$ hydrochloric acid when titrated with phenolphthalein as indicator. But the same amount of the solution, when titrated with methyl orange as indicator required 30 ml. of the same acid. Calculate the amount of potassium hydroxide, KOH, and sodium carbonate, Na_2CO_3, in grams.

Phenolphthalein gives the full titre value of KOH solution $+\frac{1}{2}$ the titre value of $Na_2CO_3 \equiv 20$ ml. of $N/20$ HCl.

Methyl orange gives the full titre value of KOH+full titre value of $Na_2CO_3 \equiv 30$ ml. of $N/20$ HCl.

$\therefore$ The difference (30—20=10) ml. of $N/20$ HCl corresponds to $\frac{1}{2}$ the titre value of Na_2CO_3 solution.

The strength of Na_2CO_3 solution$\equiv 2\times 10$ or 20 ml. of $N/20$ HCl.

And the strength of KOH solution$\equiv 20-10$ or 10 ml. of $N/20$ HCl.

Now since 20 ml. of $N/20$ HCl$\equiv$20 ml. of $N/20$ Na_2CO_3, the amount of Na_2CO_3 (eq.wt.=53) in grams

$$=\frac{53}{20}\times\frac{20}{1000}=0{\cdot}052 \text{ g.}$$

Again, since 10 ml. of $N/20$ HCl$\equiv$10 ml. of $N/20$ KOH, the amount of KOH (eq.wt.=56) in grams

$$=\frac{56}{20}\times\frac{10}{1000}=0{\cdot}028 \text{ g.}$$

No. 2.

Estimation of sodium carbonate and sodium bicarbonate in a mixture of both.

Titrations are done against a standard solution of sulphuric acid ($N/10$) using phenolphthalein as indicator first, and then completing the titration with methyl orange.

Phenolphthalein does not act on sodium bicarbonate and, therefore, the titre value corresponds to the stage :

$$Na_2CO_3 \rightarrow NaHCO_3.$$

When methyl orange is added at this stage, we get the complete titre value :

$$NaHCO_3 \rightarrow Na_2SO_4.$$

Example—20 ml. of a mixture, when titrated against $N/10$ sulphuric acid, the end point with phenolphthalein was reached at 5·0 ml. and at this stage, methyl orange was added, the quantity of acid further required for the end point was 20.4 ml.

$\therefore$ Amount of Na_2CO_3 corresponds to $2\times 5{\cdot}0=10{\cdot}0$ ml. of $N/10$ acid and the amount of $NaHCO_3$ to $[(5{\cdot}0+20{\cdot}4)-10{\cdot}0]$ ml. or 15·4 ml. of the acid.

Numerical—25 ml. of a mixed solution of sodium carbonate and bicarbonate, required 12 ml. of $N/20$ HCl when titrated in presence of phenolphthalein, but 25 ml. of the same when titrated separately in presence of methyl orange required 30 ml. of $N/20$ HCl. Calculate the amount of anhydrous Na_2CO_3 and $NaHCO_3$ in grams per litre of the solution.

(i) The titre value with phenolphthalein corresponds to half the value of Na_2CO_3 *alone* ($NaHCO_3$ gives no indication)$\equiv$12 ml. of $N/20$ HCl.

(ii) The titre value with methyl orange corresponds to full Na_2CO_3 and $NaHCO_3$$\equiv$30 ml. of $N/20$ HCl.

From (i), the full value of Na_2CO_3

$$\equiv 12\times 2=24 \text{ ml. of } N/20 \text{ HCl}$$
$$\equiv 24 \text{ ml. of } N/20\ Na_2CO_3.$$

This amount is present in 25 ml. of the mixed solution, hence per litre, it corresponds to $\frac{24\times 1000}{25}$ ml. of $N/20$ Na_2CO_3.

$$=\frac{53}{20}\times\frac{24\times 1000}{25}\times\frac{1}{1000} \text{ g. of } Na_2CO_3$$
$$=2.544 \text{ g. of } Na_2CO_3.$$

From (ii), now, the full value of $NaHCO_3$ *alone* would correspond to (30—12$\times$2=6) ml. of $N/20$ HCl.

$$=6 \text{ ml. of } N/20\ NaHCO_3$$

This amount is present in 25 ml. of the mixed solution. The equivalent weight of $NaHCO_3$ is 84, and hence, the amount of $NaHCO_3$ is:

$$=\frac{6\times 1000}{25}\times\frac{84}{20}\times\frac{1}{1000}$$
$$=1.008 \text{ g. of } NaHCO_3.$$

Estimation of ammonia in ammonium salts.

The ammonia expelled by heating the ammonium compound with a concentrated solution of sodium hydroxide is absorbed in a known volume of a standard acid, usually sulphuric, and the excess of acid is determined by titration with a standard solution of alkali.

For practical experiments, one can weigh out about 4 g. of ammonium chloride accurately, and place it in a distillation flask. The flask is fitted up with a dropping funnel for caustic soda solution, and another delivery tube (it may be a simple bent tube connected with a pipette), which dips into the standard solution of dilute sulphuric acid placed in a conical flask (take 100 ml. of N-sulphuric acid). Drop a strong solution of caustic soda from the dropping funnel and distil out the evolved ammonia. Make up the volume of the distillate to 250 ml. Take 10 ml. of the made up solution and titrate it with $N/2$ NaOH solution.

$$NH_4Cl+NaOH=NaCl+NH_3+H_2O.$$

Alternate method—It depends upon decomposing the salt by boiling it with a known volume of standard sodium hydroxide solution; the boiling is continued until no more ammonia escapes with steam. In this experiment, sodium hydroxide must be taken in excess. A portion of the alkali would be used up in the decomposition of the ammonium salt and the excess left over is titrated with a standard solution of an acid.

From the equation given above, it will be seen that 17·00 g. NH_3 correspond to 40 g. of NaOH.

EXAMPLES

(*i*) 2.50 g. of an ammonium salt were heated with an excess of caustic soda, and the evolved ammonia was absorbed in 60 ml. of *N*-sulphuric acid solution, the excess of the acid required 14 ml. of *N* NaOH for titration. Calculate the percentage of NH_3 in the ammonium salt.

$$14 \text{ ml. of } N \text{ NaOH} \equiv 14 \text{ ml. of } N \text{ } H_2SO_4.$$

Thus, *N* sulphuric acid used up = 60—14 ml. = 46 ml.

$\equiv$ 46 ml. *N* NaOH.

$\equiv$ 46 ml. *N* NH_3.

The amount of NH_3 in the salt is $\frac{17 \times 46}{1000}$ g.

$= 0·782$ g.

The percentage of NH_3 in the salt $\frac{0·782 \times 100}{2·50} = 31·28$.

(*ii*) 2·26 g. of an ammonium salt were treated with 50 ml. of normal caustic soda solution, and boiled till no more of ammonia was given off. The excess of the alkali solution left over was titrated with *N* sulphuric acid. The volume of the acid required was 10 ml. Find out the percentage of NH_3 in the salt and also the percentage of ammonium radical, NH_4.

$$10 \text{ ml. of } N \text{ } H_2SO_4 \equiv 10 \text{ ml. of } N \text{ NaOH.}$$

The amount of alkali used up (50—10) ml. = 40 ml.

40 ml. of *N* NaOH $\equiv$ 40 ml. of *N* $NH_3 \equiv$ 10 ml. of *N* NH_4.

The equivalent weight of NH_3 is 17 and of NH_4 is 18.

40 ml. of *N* NH_3 contains $\frac{17 \times 40}{1000}$ g. = 0.680 g. of NH_3.

Therefore, the salt contains $\frac{0.680\times 100}{2.26}=30.09\% NH_3$.

Similarly, it contains $\frac{0\cdot 720\times 100}{2.26}=31.86\%$ of NH_4.

Estimation of nitrates and nitrites by reducing them to ammonium salts by Devarda's alloy—All the nitrites and nitrates are reduced by Devarda's alloy to ammonia. The alloy has the composition (Al 45, Cu 50, and Zn 5). The given weighed sample of the nitrate is treated with this alloy in presence of a strong solution of caustic soda, and heated. The nitrate is reduced to ammonia.

$$3NaOH+Al=Al(ONa)_3+3H.$$
$$NaNO_3+8H=NaOH+NH_3+2H_2O.$$

The ammonia is distilled and absorbed in a known volume of a standard solution of an acid. The excess of the acid is then titrated with a standard alkali solution.

From the reactions, it is clear that :—

$$\underset{85\cdot 0}{NaNO_3}\equiv\underset{17}{NH_3}\equiv\underset{36\cdot 46}{HCl}\equiv\underset{40\cdot 03}{NaOH}$$

Example—1.219 g. of sodium nitrate sample was reduced by Devarda's alloy, and the ammonia evolved was absorbed in 100 ml. of $N/10$ HCl solution. The acid was then transferred to a flask and made up to 250 ml. ; 50 ml. of the acid when titrated with $N/20$ NaOH required 13·4 ml. of the alkali. Find out the percentage of sodium nitrate in the sample titrated with a standard alkali solution.

The total acid left unused$\equiv 13.4\times 5=67.0$ ml. of $N/20$ NaOH
$\equiv 33.5$ ml. of $N/10$ HCl.

Therefore, the acid used up$=(100\text{-}33\cdot 5)$ or 66·5 ml.
66.5 of ml. $N/10$ HCl$\equiv$66.5 ml. of $N/10$ NaOH.
$\equiv$66.5 ml. of $N/10$ $NaNO_3$.

$$=\frac{66\cdot 5\times 8\cdot 5}{1000}\text{ g. of } NaNO_3$$
$$=0.5652\text{ g. of } NaNO_3.$$

Thus the precentage of $NaNO_3$ in the sample is $\frac{0.5652\times 100}{1.219}$
$=46.37$.

SECTION II

Oxidation and Reduction

Oxidation reactions.—Potassium dichromate and potassium permanganate contain oxygen which is made available to various

substances for oxidation. But these substances lose this available oxygen only in the presence of a reducing substance (a substance capable of receiving oxygen). The reaction is best studied in the presence of dilute sulphuric acid. During the process of oxidation, potassium dichromate is itself reduced to potassium and chromium salts and potassium permanganate to potassium and manganous salts. Thus in presence of sulphuric acid, we have:

$$K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O.$$
$$2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O.$$

Three atoms of oxygen are available from one molecule of $K_2Cr_2O_7$ and five atoms of oxygen from two molecules of $KMnO_4$ for the purpose of oxidation.

Equivalent weights.—In order to prepare standard solutions, we require the equivalent weights of these oxidising substances. Here the gram-equivalent weight of a compound is taken to be that weight which shall oxidise one gram-atom (1.088 g.) of hydrogen or will supply 8.000 grams of oxygen for oxidation.

Oxidation—It is the increase in the positive valency of an element or radical by the addition of oxygen, chlorine or some other atom or radical which can constitute anions or electronegative radicals. *Oxidation* is also defined as a process which results in the loss of one or more electrons by atoms or ions. An *oxidising agent* is one that *gains* electrons and is reduced to a lower valency condition. When sodium burns in chlorine, sodium is oxidised, it loses one electron:

$$2Na+Cl_2\rightarrow 2Na^+Cl^-$$
$$Na-\epsilon=Na^+$$

Reduction—It is the decrease in the positive valency (or increase in the negative valency) by the removal of oxygen or some electronegative atom or radical, or by the addition of an atom or radical which can constitute cations. *Reduction* is again a process which results in a gain of one or more electrons by atoms or ions. A *reducing agent* is one that loses electrons and becomes oxidised to a higher valency condition.

Oxidation number—Oxidation number of an element is a number which applied to that element in a particular compound, indicates the amount of oxidation or reduction which is required to covert one atom of the element from the *free* state to that state with which it is associated in the compound. If the oxidation is necessary to bring out this change, the oxidation number is positive. Again, if reduction is necessary, the oxidation number is negative.

Rules for oxidation number.—The following considerations would help in determining the *oxidation number* (abbreviation O.N.)

(*i*) The O.N. of free or uncombined element. is zero, as of elementary C,S,Cl_2 etc., we shall write is C°, S°, Cl_2° etc.

(*ii*) Except in hydrides, the O.N. of hydrogen in combination is +1,

(*iii*) The O.N. of oxygen in combination is −2.

(*iv*) The O.N. of a *metal* in combination is positive.

(*v*) The O.N. of a radical or an ion is that of its electrovalency with correct sign, + or −, attached, *i.e.*, is equal to its charge.

(*vi*) The O.N. of a compound is always zero and is determined by the sum of the O.N.'s of the individual atoms, each multiplied by the number of atoms of the element in one molecule.

Examples—

1. What is the O. N. of S in H_2S?

O. N. of H_2S is zero (rule *vi*)
O. N. of H is +1 (rule *ii*)
∴ O. N. of 2H is +2
+2 + (O.N. of S) = 0
∴ O. N. of S = −2.

2. What is the O. N. of N in HNO_3?

O. N. of H + O. N. of N + 3 × (O. N. of O) = 0.
1 + O. N. of N + (3 × −2) = 0
∴ O. N. of N. = +6 − 1 = +5

3. What is the O. N. of Mn is $KMnO_4$?

O. N. of K is +1; O. N. of O_4 is 4 × (−2) = −8
∴ +1 + (O. N. of Mn) − 8 = 0.
∴ O. N. of Mn = +7.

4. What is the O. N. of Cr in K_2CrO_4 and $K_2Cr_2O_7$?

(*i*) In K_2CrO_4—
O. N. of 2K is 2 × (+1) = 2
O. N. of O_4 is 4 × (−2) = −8
∴ 2 + (O. N. of Cr) − 8 = 0
∴ O. N. of Cr = 8 − 2 = +6.

(*ii*) In $K_2Cr_2O_7$—
2 + 2(O.N. of Cr) + 7 × (−2) = 0
∴ 2(O. N. of Cr) = 14 − 2 = +12
∴ O. N. Cr = +6.

Thus O. N. of Cr in both K_2CrO_4 and $K_2Cr_2O_7$ is $+6$., that is, chromium is in the same oxidation state in these compounds.

Now we have seen that one gram-molecule of potassium dichromate in acidic solutions supplies 3 gram atoms of oxygen for oxidation, *i.e.*, the oxygen which can oxidise 6 gram-atoms (6.043g.) of hydrogen. So that the equivalent weight will be $\frac{K_2Cr_2O_7}{6}$, because this will be the amount which will oxidise 1 gram-atom (1.008 g.) of hydrogen.

$\therefore$ Equivalent weight of $K_2Cr_2O_7$ for normal solution is: $\frac{K_2Cr_2O_7}{6} = \frac{294.18}{6} = 49.03$.

Similarly, two molecules of potassium permanganate in presence of acids supply 5 atoms of oxygen for oxidation, *i.e.*, the oxygen which can oxidise 10 gram-atoms (10.08 g.) of hydrogen. So that the equivalent weight will be $\frac{2KMnO_4}{10}$ because this will be the amount which will oxidise 1 gram-atom (1·008 g.) of hydrogen.

$\therefore$ Gram-equivalent weight of potassium permanganate for normal solution is:

$$\frac{2KMnO_4}{10} = \frac{2 \times 158.03}{10} = \frac{316.06}{10} = 31.606 \text{ g.}$$

The reaction may be simplified as:

$$2KMnO_4 = K_2O + 2MnO + 5O.$$

$$H_2C_2O_4 + O = H_2O + 2CO.$$

No. 3.

Titration of oxalic acid with potassium permanganate

Reaction—Potassium permanganate in presence of dilute sulphuric acid oxidises oxalic acid to carbon dioxide and water. The following reaction takes place:

$$2KMnO_4 + 5C_2O_4^{=} + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 5H_2O.$$

The ionic equation is:

$$2MnO_4^{-} + 5C_2O_4^{=} + 16H^{+} = Mn^{++} + 10CO_2 + H_2O.$$

Suppose one is required to determine the exact strength of an oxalic acid solution supplied, the approximate strength of which is given to be about *N*/20. This can be done by titrating it against a potassium permanganate solution of known strength (app. *N*/20)

in presence of dilute sulphuric acid. Now it is difficult to prepare a solution of permanganate of exactly the desired strength and so it has got to be standardised. This is done by titrating it against a solution of oxalic acid of known strength which can easily be prepared.

(*i*) *Preparation of an oxalic acid solution of known strength* (accurate but near about $N/20$) —As has already been shown, a normal solution of oxalic acid contains 63 g. of oxalic acid per litre. Hence for $N/20$ solution, we shall require 63/20 g.=3·15 g. oxalic acid per litre. So that if we are preparing the solution in a 100 ml. measuring flask (which is generally the case), we require

$$\frac{3\cdot15}{10} \text{ g.}=0.3150 \text{ g. of oxalic acid.}$$

Now accurately weigh out about 0.3150 g. of pure A. R. quality oxalic acid, dissolve it in water and raise the solution to 100 ml. in the measuring flask. Suppose you have weighed m g. for 100 ml. solution, then the strength of the prepared solution is $\frac{N\times 10m.}{63}$

(*ii*) *Preparation of $KMnO_4$ solution of approximate strength $N/20$* —A normal solution of $KMnO_4$, as has been shown, contains 31.6 g. of $KMnO_4$ per litre, so that for $N/20$ solution, we require 1·58 g. per litre.

Hence, weigh out about 1.58 g. of $KMnO_4$ and dissolve it in about a litre of water. This is $KMnO_4$ solution of about $N/20$ strength. This solution is generally supplied, and is to be standardised.

(*iii*) *Standardising the solution of permanganate against the prepared oxalic acid solution*—Take permanganate solution in the burette. Now take 10 ml. of the prepared oxalic acid solution in a clean beaker by means of a pipette and add to it about 10 ml. of dilute sulphuric acid. Warm it to 90° or so. Now add to it, the permanganate solution gradually till a light pink colour just appears. Repeat this process two or three times and take the concordant values as the value requird per 10 ml. of oxalic acid solution. The strength of the permanganate solution is calculated as follows:

Amt. of oxalic acid weighed$=m$ g.

Oxalic acid is dissolved in water and raised to 100 ml.

$\therefore$ Strength of oxalic acid solution$=\frac{N}{63}\cdot 10m=\frac{N}{6\cdot3}\cdot m$

Vol. of oxalic acid taken for titration$=10$ ml.

Titre value of $KMnO_4 = V_1$ ml.

Let the strength of $KMnO_4$ solution be $\frac{N}{x}$.

Strength of $KMnO_4 \times$ vol. = strength of oxalic acid $\times$ vol.

$$\therefore \qquad \frac{N}{x} \times V_1 = \frac{N}{6.3} m \times 10$$

$$\therefore \qquad \frac{N}{x} = \frac{N}{6.3} \times m \times \frac{10}{V_1}.$$

(*iv*) *Determining the strength of the given oxalic acid solution*—Now take 10 ml. of the given oxalic acid solution in a beaker, add to it about 10 ml. of dilute sulphuric acid and heat. Add permanganate solution from the burette till a permanent light pink colour is obtained. Repeat the process till you get concordant values.

Volume of unknown oxalic acid = 10 ml.

Titre value of $KMnO_4$ for this = V_2.

Let the strength of oxalic acid (unknown) be $\frac{N}{y}$.

Strength of unkown oxalic acid $\times$ vol.

= strength of $KMnO_4 \times$ vol.

$$\therefore \qquad \frac{N}{y} \times 10 = \frac{N \times m \times 10}{6.3 \times V_1} \times V_2$$

$$\therefore \qquad \frac{N}{y} = \frac{N \times m}{6.3} \times \frac{10}{V_1} \times \frac{V_2}{10}$$

$$= \frac{N \times m}{6.3} \times \frac{V_2}{V_1}$$

If you are required to calculate the value in grams per litre, substitute 63 for N and you get the amount. Thus the amount of oxalic acid in grams per litre in the given solution is:

$$\frac{63 \times m}{6.3} \times \frac{V_2}{V_1} = 10m \times \frac{V_2}{V_1}.$$

Numerical—1. Find out the concentration of an oxalic acid solution in grams of anhydrous acid per litre, 20 ml. of which require 17 ml. of $N/25$ potassium permanganate solution.

Strength of oxalic acid $\times$ volume in ml. = strength of $KMnO_4$ $\times$ volume in ml.

$$\therefore \quad \frac{N}{x}\times 20=\frac{N}{25}\times 17$$

$$\therefore \quad \frac{N}{x}=\frac{N}{25}\times\frac{17}{20}=\frac{N}{29.41}$$

Since anhydrous oxalic acid, $H_2C_2O_4$, has equivalent wieght 45, the strength of the solution is $\frac{45}{29.41}$ g. per litre.

$=1.530$ g. per litre.

2. Find out the percentage of oxalate, C_2O_4, in a given sample of an oxalate salt, of which when 0.375 g. dissolved in 100 ml. required 12 ml. of $N/20$ potassium permanganate solution for 10 ml. of the oxalate solution.

The strength of oxalate solution

$$=\frac{N}{20}\times\frac{12}{10}=\frac{N}{16.66}$$

The equivalent of C_2O_4 radical is 44.

$\therefore$ the strength of the solution $=\frac{44}{16.66}$ g. per litre, or $\frac{4.4}{16.66}$ g. per 100 ml.

Since 0.375 g. of the oxalate sample contains

$\frac{4.4}{16.66}$ g. of the oxalate,

$\therefore$ 100 g. of the oxalate sample contains

$$\frac{4.4}{16.66}\times\frac{100}{0.375}\text{ g.}=70.4\text{ g.}$$

$\therefore$ the percentage of $C_2O_4=70.4$

No. 4

Titration of ferrous ammonium sulphate and potassium permanganate.

Suppose you are given a solution of ferrous ammonium sulphate of strength approximately $N/30$ and you are required to determine its exact strength. This can be done by titrating it against a potassium permanganate solution of known strength (about $N/30$) in presence of dilute H_2SO_4. The permanganate solution, in turn, is standardised against a standard oxalic acid solution as before or against a standard ferrous ammonium sulphate which can easily be prepared to an accuracy by direct weighing.

(*i*) *Perparation of ferrous ammonium sulphate solution of a known exact strength* (about $N/30$)—A normal solution of ferrous ammonium sulphate contains 302.1 g. of the salt per litre. Therefore, $N/30$ solution will require $\frac{392.1}{30}$ g.=13.07 g. per litre. Hence if the solution is to be prepared in a 100 ml. measuring-flask (which is generally the case) $\frac{13.07}{10}$ =1.307 g. of ferrous ammonium sulphate are required.

Weigh out exactly about 1.307 g. of pure A. R. quality ferrous ammonium sulphate, dissolve it in water, add about 10 ml. of dilute H_2SO_4 to make the solution clear and prevent hydrolysis and make it up to 100 ml. in the measuring flask.

Suppose *m g.* of ferrous ammonium sulphate has been weighed and the solution made up to 100 ml. then the strength of this solution is $\frac{N\times 10m}{392.1}=\frac{N}{39.21}\,m$.

(*ii*) *Preparation of about $N/30$ $KMnO_4$ solution*—Weigh out about $\frac{31\cdot 6}{30}=1\cdot 0533$ g. of $KMnO_4$ and dissolve it in about a litre of water. This will give about $N/30$ $KMnO_4$ solution.

In this reaction, potassium permanganate in presence of dilute sulphuric acid oxidises the ferrous salt to ferric. The following reaction takes place:—

$$2KMnO_4+10FeSO_4+8H_2SO_4=5Fe_2(SO_4)_3+2MnSO_4+K_2SO_4+8H_2O.$$

Or when simplified :

$$2KMnO_4=K_2O+MnO+5O.$$
$$10FeSO_4+5H_2SO_4+5O=Fe_2(SO_4)_3+5H_2O.$$

The ionic equation is :

$$MnO_4^-+5Fe^{++}+8H^+=Mn^{++}+5Fe^{+++}+4H_2O$$

(*ii*) *Standardising the $KMnO_4$ solution against the prepared ferrous ammonium sulphate solution.* Take permanganate solution in the burette. Now take 14 ml. of the prepared ferrous ammonium sulphate solution in a clean beaker by means of a rinsed pipette and add to it about 10 ml. of dilute H_4SO_4. Add to it the permanganate solution gradually till light pink colour just appears. Repeat this process two or three times, till you get concordant values. This is the volume of permanganate solution which can

Let N/x be the strength of permanganate solution, and for 10 ml. of the ferrous ammonium sulphate solution, let the titre value of $KMnO_4$ be v_1 ml.

$$\therefore \quad \frac{N}{x} \times v_1 = \frac{N}{39 \cdot 21} \times m \times 10.$$

$$\therefore \quad \frac{N}{x} = \frac{N \times m}{39 \cdot 21} \times \frac{10}{v_1}.$$

(*iv*) *Determining the strength of an unknown ferrous ammonium sulphate solution*—Take 10 ml. of the unknown ferrous ammonium sulphate solution in a beaker and add to it about 10 ml. of dilute H_2SO_4. Titrate it against permanganate solution standardised. Let v_2 be the titre value of permanganate solution for 10 ml. of the unknown ferrous ammonium sulphate solution and N/y be the strength of the unknown solution.

$$\therefore \quad \frac{N}{y} \times 10 = \text{Strength of } KMnO_4 \times v_2$$

$$\therefore \quad \frac{N}{y} \times 10 = \frac{N \times m}{39 \cdot 21} \times \frac{10}{v_1} \times v_2$$

$$\therefore \quad \frac{N}{y} = \frac{N \times m}{39 \cdot 21} \times \frac{10}{v_1} \times \frac{v_2}{10}$$

$$= \frac{N \times m}{39 \cdot 21} \times \frac{v_2}{v_1}.$$

This is the required strength.

If the amount of ferrous salt present per litre has to be calculated, put 392.1 for N and get the result.

$$= \frac{392 \cdot 1 \times m}{39 \cdot 21} \times \frac{v_2}{v_1} \text{ g.}$$

$$= 10m \times \frac{v_2}{v_1} \text{ g.}$$

Numerical—20 ml. of a ferrous sulphate solution required 10 ml. of a potassium permanganate solution. This permanganate solution when standardised against 20 ml. of $N/20$ oxalic acid solution gave the titre value 17 ml. Find out the strength of ferrous sulphate in terms of $FeSO_4 . 7H_2O$ per litre.

The strength of $KMnO_4$ solution × vol.

$$\therefore \quad \frac{N}{x} \times 16 = \frac{N}{20} \times 20$$

$$\therefore \quad \frac{N}{x} = \frac{N}{16} \qquad (KMnO_4)$$

The strength of ferrous sulphate $= \frac{N}{y} \times$ vol.

= the strength of $KMnO_4 \times$ vol.

$$\frac{N}{y} \times 20 = \frac{N}{16} \times 18$$

$$\frac{N}{y} = \frac{N}{16} \times \frac{18}{20} = \frac{N}{17 \cdot 77}$$

The equivalent weight of $FeSO_4 . 7H_2O = 278$

$\therefore$ The strength of the solution

$$= \frac{278}{17 \cdot 77} = 15 \cdot 64 \text{ g. per litre.}$$

No. 5

Titration of ferrous ammonium sulphate and potassium dichromate (external indicator method)

In this reaction, potassium dichromate in presence of sulphuric acid oxidises ferrous salt to ferric as follows;

$$6[FeSO_4.(NH_4)_2SO_4.6H_2O] + K_2Cr_2O_7 + 7H_2SO_4$$
$$= 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 6(NH_4)_2SO_4 + 43H_2O.$$

If we do not consider $(NH_4)_2SO_4.6H_2O$ portion of ferrous ammonium sulphate, as it does not take part in the reaction, we find that the actual reaction is :

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O.$$

This may be further simplified thus :

$$K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O.$$
$$6FeSO_4 + 3H_2SO_4 + 3O = 3Fe_2(SO_4)_3 + 3H_2O.$$

The ionic equation is :

$$6Fe^{++} + Cr_2O_7^{--} + 14H^{+} = 6Fe^{+++} + 2Cr^{+++} + 7H_2O.$$

As potassium dichromate solution is reddish-yellow in colour

just an excess of dichromate has been added to the ferrous salt) cannot be easily seen. In this respect it is different from $KMnO_4$ titration where the end point is indicated by the light pink colour of $KMnO_4$. We have, therefore, to use an indicator in this case, and that too *external*.

Indicator—(*a*) A freshly prepared solution of potassium ferricyanide is used as an *external indicator* (if it were used as an internal indicator it would react with ferrous sulphate forming a complex) Potassium ferricyanide gives a blue precipitate with ferrous salts but not with ferric, so that as long as ferrous salt is there, a drop of reaction solution touched with a drop of the indicator will give a a blue colour but as soon as the whole of it has been oxidised, no more blue colour will be obtained.

(*b*) The diphenylamine sulphonate may be used as an *internal* indicator. So long as ferrous ions are present, it is not oxidised but the moment, the dichromate has been added in excess, the diphenylamine is oxidised by dichromate, and a greenish blue colour appears.

Prepare the indicator by dissolving 0·1 g. of diphenylamine in 10 ml. of concentrated sulphuric acid.

Add 4 to 6 drops of the indicator for each titration, and also add 35 ml. of a mixture of sulphuric and phosphoric acids (made up by adding 10 ml. of syrup phosphoric acid and 10 ml. of concentrated sulphuric acid to 50 ml. of water and diluting to 100 ml. This mixture is added to remove ferric ions). Now run in the standard dichromate solution until a greenish blue colour appears.

To find out the strength of a given dichromate solution.

Now coming to the actual experiment, you may be asked to determine the exact strength of a potsssium dichromate solution, the strength of which is near about $\frac{N}{30}$. This can be done by titrating it against a ferrous ammonium sulphate solution of known strength (app. $\frac{N}{30}$) in presence of dilute H_2SO_4. The ferrous ammonium sulphate solution in turn can be standardised against a $K_2Cr_2O_7$, solution of known strength which one shall prepare himself.

(*i*) *Preparation of a dichromate solution of a known strength.* (app. $\frac{N}{30}$)—A normal solution of $K_2Cr_2O_7$ contains 49·03 g. of $K_2Cr_2O_7$ per litre. Hence for $\frac{N}{30}$ solution, we shall require $\frac{49\cdot03}{30}=1\cdot6343$ g. of $K_2Cr_2O_7$ per litre. But if the solution is to be prepared

in a 100 ml. measuring flask (which is generally the case), we require $\frac{1\cdot6343}{10}=0\cdot1634$ g. of $K_2Cr_2O_7$.

Weigh out exactly about 0.1634 g. of pure A. R. quality $K_2Cr_2O_7$, dissolve it in water and make the solution up to 100 ml. in the measuring flask. Suppose you have weighed m g. for 100 ml. of the solution, then the strength of this solution is $\frac{N}{49\cdot03}\times10m$

$=\frac{N}{4\cdot903}m.$

(*ii*) *Preparation of ferrous ammonium sulphate solution of app. strength N/30.* Weigh out about $\frac{392\cdot1}{30}=13\cdot07$ g. of ferrous ammonium sulphate, dissolve it in water, *add some dilute* H_2SO_4 to make the solution clear and prevent hydrolysis and make it up to a litre. This will give about $N/30$ ferrous ammonium sulphate solution.

(*ii*) *Standardising the ferrous ammonium sulphate solution against the prepared potassium dichromate solution.* This titration is different from others as the intermediate solution is taken in beaker and *not in burette* as in other cases. The reason is that during the progress of the titration, we have to examine the contents of the beaker for the presence or absence of ferrous ions by means of potassium ferricyanide; and the end point is taken as the disappearance of the blue colour which is more sensitive than the reappearance.

Take the prepared potassium dichromate solution in the burette. Now take 10 ml. of ferrous ammonium sulphate solution in a clean beaker and add to it about 10 ml. of dilute H_2SO_4. On a clean white tile (or a porcelain piece), put by means of a glass rod a number of drops of the freshly prepared solution of potassium ferricyanide which is to be used as indicator in order to study the progress of titration. Now add $K_2Cr_2O_7$ solution from the burette gradually, 1 ml. at a time and after adding each ml., put a drop of the contents of the beaker by means of a glass rod over a drop of the indicator on the tile. After touching the indicator the rod should be cleaned with distilled water before dipping it again into the beaker. Thus find at what point the blue colour does not appear. Suppose it appears at 9 ml. and does not appear at 10 ml.; we come to the conclusion that 9 ml. of dichromate solution are too little and 10 ml. are too much for 10 ml. of ferrous ammonium sulphate solution.

Take 10 ml. of ferrous ammonium sulphate solution again in a clean beaker and add about 10 ml. of dilute H_2SO_4 to it. Now run in 9 ml. of dichromate solution from the burette and this time,

test the solution after the addition of each 0·1 ml. of the dichromate solution whether the colour appears or not with the indicator. Thus you will bring down the range of accuracy to 0·1 ml. Suppose the blue colour appears at 9·6 ml. and does not appear at 9·7 ml., we come to the conclusion that 9·6 ml. are too little and 9·7 ml. are too much for 10 ml. of ferrous ammonium sulphate.

Again take 10 ml. of ferrous ammonium sulphate solution in a beaker and add to it about 10 ml. of dilute H_2SO_4. Run in 9·5 ml. of $K_2Cr_2O_7$ solution from the burette and this time see after the addition of each drop whether the blue colour appears with the indicator. Thus you will get exact end point this time. Repeat the process by again adding 9·5 ml. of $K_2Cr_2O_7$ and taking the end point as before, till you get concordant results.

Let the volume of $K_2Cr_2O_7$ solution for 10 ml. of ferrous ammonium sulphate solution as found above be v ml. and let the unknown strength of ferrous salt be N/x.

$\therefore$ $N/x \times 10$ ml. = Strength of dichromate $\times v$ ml.

$$\frac{N}{x} \times 10 = \frac{N}{4\cdot903} m \times v_1$$

$$\frac{N}{x} = \frac{N \times m}{4\cdot903} \times \frac{v_1}{10}$$

(*iv*) *Determination of the strength of given unknown potassium dichromate solution*—Clean your burette, rinse it with the given $K_2Cr_2O_7$ solution and fill it up with this solution. Take 10 ml. of the standardised ferrous ammonium sulphate in a clean beaker, add to it about 10 ml. of dil. H_2SO_4 and find out, as before (*iii*), the titre value of the given unknown $K_2Cr_2O_7$ solution for 10 ml. of ferrous ammonium sulphate. Let this be v_2 ml.

Let the strength of the unknown dichromate solution be N/y.

$\therefore$ $N/y \times v_2$ ml. = Strength of ferrous solution $\times$ 10 ml.

$$= \frac{N \times m}{4\cdot903} \times \frac{v_1}{10} \times 10$$

$$\frac{N}{y} = \frac{N \times m}{4\cdot903} \times \frac{v_1}{v_2}$$

This is the required strength.

If the amount per litre has to be calculated, we put 49·03 for N and get the result :

$$K_2Cr_2O_7 \text{ in g. per litre} = \frac{49\cdot03 \times m \times v_1}{4\cdot903 \times v_2} \text{ g. per litre.}$$

$$= 10m \times v_1/v_2 \text{ g. per litre.}$$

Numerical—Calculate the strength of a potassium dichromate solution, 20 ml. of which require 22 ml. of a given ferrous ammonium sulphate solution, 20 ml. of this ferrous salt solution required 15 ml. of $N/20$ potassium permanganate solution.

The strength of ferrous solution $N/x \times$ vol.

$$= \text{the strength of } KMnO_4 \times \text{vol.}$$

$$\therefore \quad N/x \times 20 = N/20 \times 15$$

$$\therefore \quad N/x = \frac{N}{20} \times \frac{15}{20} = \frac{N}{26 \cdot 66}$$

The strength of $K_2Cr_2O_7$, $N/y \times$ vol.

$$= \text{the strength of ferrous solution} \times \text{vol.}$$

$$\therefore \quad N/y \times 20 = N/26 \cdot 66 \times 22$$

$$\therefore \quad \frac{N}{y} = \frac{N}{26 \cdot 66} \times \frac{22}{20} = \frac{N}{24 \cdot 24}$$

The equivalent weight of $K_2Cr_2O_7 = 49 \cdot 03$

$\therefore$ the strength of $K_2Cr_2O_7$ solution

$$= \frac{49 \cdot 03}{24 \cdot 24} \text{ g.} = 2 \cdot 027 \text{ g. per litre.}$$

Exercise—*Find out the total amount of potassium dichromate in the volume of the solution supplied. For this purpose, prepare your own solution of potassium dichromate of about $N/30$ strength.*

Procedure—1. Prepare your own about $N/30$ solution of potassium dichromate (weighing near about 0·1634 g. of $K_2Cr_2O_7$ accurately in a 100 ml. flask). (*Known solution*).

2. Raise the *whole* of the given volume of the unknown dichromate solution to 100 ml. volume in a 100 ml. flask. (*Unknown solution*).

Note—It is always preferred to prepare both the 'known' and 'unknown' solutions in the same 100 ml. flask to minimise the error in the graduation of flasks.

3. Use an intermediate solution of ferrous ammonium sulphate of about $N/30$ strength for titration. For each titration, pipette out 10 ml. of this solution in a clean beaker. Use a solution of potassium ferricyanide as an *external indicator*.

Potassium dichromate solutions are to be kept in burette.

Complete the titrations first with your prepared standard "known" dichromate solution, and note down the titre readings. Then complete the titrations with the "unknown" dichromate solution.

Calculations—

The amount of potassium dichromate weighed for 100 ml. solution = m g.

The volume of the "known" dichromate solution for titrating 10 ml. of ferrous solution $= v_1$ ml.

The volume of the "unknown" dichromate solution for titrating the same 10 ml. of the ferrous solution $= v_2$ ml.

The "unknown" solution in 100 ml. contains

$$\frac{m \times v_1}{v_2} \text{ g.}$$

Since the total volume of the supplied dichromate solution was raised to 100 ml. volume, the amount of the dichromate present in the volume of the solution supplied is also

$$\frac{m \times v_1}{v_2} \text{ g.}$$

No. 6

Potassium dichromate-ferrous salt titration (Internal indicator)

The internal indicators used are (i) 1% solution of diphenylamine in conc. sulphuric acid—Knop indicator, (ii) 0·2—0·3% aqueous solution of sodium diphenylamine sulphonate, or (iii) 1% solution of N-phenyl anthranilic acid. With these indicators, phosphoric acid must be added. It is known that phosphoric acid lowers the oxidation potential of the ferric-ferrous* system by forming a complex with the ferric ions. These indicators impart a green colour to the ferrous solution which deepens to a blue-green shortly before the end point. At the equivalence point, an intense purple or blue-violet coloration is obtained, which remains permanent after shaking.

Titration is done in cold. Add 6-8 drops of the indicator (preferable (*ii*), then add 5 ml. of syrup phosphoric acid. Titrate slowly with the dichromate solution; stir well until the pure green

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*If N-phenyl anthranilic acid is used as an indicator, it would not be necessary to add phosphoric acid. The colour changes from green to violet-red at the end point.

colour changes to a grey-green. Now add the dichromate solution drop by drop, until the first tinge of blue-violet appears; this tinge ought to remain permanent on shaking.

No. 7

Determination of chromium in a chromic salt.

Theory,—When a chromium salt is boiled with potassium or ammonium persulphate in presence of a little silver nitrate (catalyst), it is converted quantitatively into a dichromate. The persulphate present in excess is completely destroyed by boiling the solution for a short time. The dichromate is then titrated against a standard ferrous salt solution.

Method,—For practice, weigh out accurately about 2·5 g. chrome alum, dissolve it in 50 ml. of water. Add 20 ml. of $0 \cdot 1N$ silver nitrate solution, and then add 50 ml. of a 10% solution of ammonium or potassium persulphate. Boil the mixture for 20 minutes. Cool and dilute to 250 ml. volume in a standard flask. Titrate the dichromate solution against $N/10$ ferrous ammonium sulphate solution, using an internal or external indicator.

AVAILABLE OXYGEN FROM PYROLUSITE

The value of a manganese ore like pyrolusite for the preparation of chlorine and for various other purposes depends upon the amount of available oxygen which it contains. By "available oxygen" is meant that part of oxygen which is available for oxidation when the ore is treated with an acid;

$$MnO_2+2HCl=MnCl_2+H_2O+O.$$
$$2HCl+O=H_2O+Cl_2$$

Thus,

$$\underset{86\cdot93}{MnO_2}\equiv\underset{16}{O}\equiv\underset{70\cdot92}{2Cl}\equiv\underset{253\cdot84}{2I}\equiv\underset{126\cdot07}{H_2C_2O_4.2H_2O}\equiv\underset{392\cdot1\times2=784.2}{2Fe\ Am.\ SO_4}$$

A number of reactions may be employed to estimate the available oxygen.

(*ii*) *By the oxidation of oxalic acid*—Take about 1·5 g. of the powdered ore in a flask, and pour upon it some 50 ml. of N oxalic acid solution and 4 ml. of concentrated sulphuric acid. Heat the mixture until all the black grains have disappeared. Filter the liquid and raise it to 250 ml. in a standard flask, and determine the amount of the undecomposed oxalic acid in this solution by titrating it with $N/10$ $KMnO_4$ solution. The amount of oxalic acid oxidised by the available oxygen is then found by difference.

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

$$H_2C_2O_4 + O = H_2O + 2CO_2.$$

$$\text{Or } MnO_2 + 4H^+ + C_2O_4^{--} = Mn^{++} + 2H_2O + 2CO_2.$$

Example—1·6 g. of pyrolusite ore were treated with 50 ml. of N oxalic acid, and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 ml. in a flask. 25 ml. of this solution when titrated with $N/10$ $KMnO_4$ required 32 ml. of the solution. Find out the percentage of pure MnO_2 in the sample and also the percentage of the available oxygen.

The total acid left undecomposed = 320 ml. of $N/10$ $KMnO_4$

$\equiv$ 32 ml. of N oxalic acid.

Thus the oxalic acid used = 50—32 = 18 ml.

N oxalic acid = $\frac{1}{2}H_2C_2O_4.2H_2O \equiv \frac{1}{2}(MnO_2)$

18 ml. of N oxalic acid $\equiv$ 18 ml. of N MnO_2.

The amount of MnO_2 present in this volume

$$= \frac{1}{2}\,\frac{86\cdot93 \times 18}{1000} = 0\cdot7823 \text{ g.}$$

The percentage of MnO_2 present in the sample is, thus,

$$\frac{0\cdot7823 \times 100}{1\cdot6} = 48.9.$$

The amount of available oxygen in 0·7823 g. of pure MnO_2

$$= \frac{16 \times 0\cdot7823}{86\cdot93} = 0\cdot144 \text{ g.}$$

The percentage of available oxygen is thus

$$= \frac{0\cdot144 \times 100}{1\cdot6} = 9\cdot00.$$

(ii) *By the oxidation of ferrous ammonium sulphate*—Weigh out about 1·5 g. of the finely divided ore, and add to it a weighed quantity (say 10 g.) of the ferrous ammonium sulphate crystals. Digest the mixture with dilute sulphuric acid. Raise the solution to 250 ml. and titrate with $N/10$ potassium dichromate solution. Thus find out the amount of ferrous ammonium sulphate left unoxidised. The difference gives the amount of the ferrous salt oxidised.

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

Sample—1·5 g. of pyrolusite ore were treated with 10 g. of ferrous ammonium sulphate crystals and dilute sulphuric acid. After the reaction the solution was raised to 250 ml.; 50 ml. of this solution were titrated with $N/10$ $K_2Cr_2O_7$; titration required 10 ml. of the dichromate solution. Find out the percentage of MnO_2 in the sample.

Total Fe. am. SO_4 undecomposed$\equiv$(5×10=50) ml. of $N/10$ $K_2Cr_2O_7$.

$$=50 \text{ ml. of } N/10 \text{ Fe. am. } SO_4.$$

$$=\frac{39\cdot20\times50}{1000}\text{ g.}=1\cdot9605\text{ g.}$$

$\therefore$ Fe. am. SO_4 used=(10−1·9605) g.=8·0395 g.

But 784·2 g. of Fe. am. $SO_4 \equiv$ 86·93 g. of MnO_2

Therefore, 8·0395 g. of Fe. am. $SO_4 = \dfrac{86\cdot93\times8\cdot0395}{784\cdot2}$ g. of MnO_2.

This much of MnO_2 is present in 0·1 g. of the sample.

Hence, the percentage purity is $\dfrac{86\cdot93\times8\cdot0395\times100}{784\cdot2+1\cdot5}=59\cdot41$;

(*iii*) *By the oxidation of potassium iodide*—About 0·5 g. of the finely powdered ore, accurately weighed, is warmed with 25 ml. of concentrated hydrochloric acid, the chlorine liberated is passed through a strong solution of potassium iodide. This will set iodine free which is titrated against a standard solution of sodium thiosulphate.

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$$
$$2KI+Cl_2=2KCl+I_2$$

For calculations, see iodometry.

VOLUMETRIC ESTIMATION OF IRON IN AN ORE

The iron usually present in an ore is in the ferric condition, and sometimes in ferrous too. The ferrous iron is estimated by dissolving the ore in concentrated hydrochloric acid, and titrating a portion at once with a standard potassium dichromate solution.

To another portion of the solution, add stannous chloride solution in excess. The ferric iron would thus be reduced to ferrous :

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4$$

or

$$2Fe^{+++}+Sn^{++}=2Fe^{++}+Sn^{++++}$$

The excess of stannous chloride is oxidised by the addition of a few drops of mercuric chloride solution : $SnCl_2+2HgCl_2=SnCl_4+2HgCl$. The precipitated calomel settles down. Now the solution is titrated with a standard solution of potasssium dichromate. This gives the total iron in the ore. Subtracting from this the value of ferrous iron, one gets the value of ferric iron.

Example. 0·9 g. of an iron ore was dissolved in concentrated HCl, and the filtered solution was raised to 100 ml. in a flask. 50 ml. of the solution were titrated with $N/20$ $K_2Cr_2O_7$. The end point was reached with 16 ml. of the solution (potassium ferricyanide as indicator). Another 20 ml. of the solution were reduced with an excess of stannous chloride, the unused stannous salt was oxidised with mercuric chloride, and the whole when titrated with the same dichromate solution required 24 ml. for the end point. Find out the percentage of ferrous and ferric in the ore.

Ferrous iron in 0·9 g. of the ore$\equiv(2\times16=32)$ ml. of $N/20$ $K_2Cr_2O_7=32$ ml. of $N/20$ Fe (ous) iron.

$$=\frac{32\times55\cdot83}{1000\times20}\text{g. iron}=0\cdot08933\text{ g.}$$

The percentage of ferrous iron is thus 9·925.

The total iron in 0·9 g. of ore$\equiv(5\times24=120)$ ml. of $N/20$ $K_2Cr_2O_7$

$$=120\text{ ml. of }N/20\text{ Fe (ous) iron.}$$

$$=\frac{120\times55\cdot84}{1000\times20}=0\cdot335\text{ g. of iron.}$$

Ferric iron is, therefore, 0·335−0·08933 or 0·2457 g.

Thus, the percentage of ferric iron in the ore is 27·30.

N.B.—In these estimations, ferric iron may be reduced by sulphur dioxide, or by zinc (or zinc amalgam) and sulphuric acid, and the titration may be done with standard potassium permanganate solutions also.

Estimation of iron in an iron wire—Take 1 g. of clean pianoforte wire, and treat it with 100 ml. of dilute sulphuric acid (add a few crystals of sodium carbonate to expel air from the flask) in a round-bottom flask. Gently heat the flask. When the wire is completely dissolved, transfer the solution to a 250 ml. standard flask, and titrate iron (which exists as ferrous sulphate) with a standard solution of $KMnO_4$ for $K_2Cr_2O_7$.

Volumetric estimation of manganese in an ore—Pattinson's method—When a solution containing iron, zinc and manganese salts is treat-

ed with bromine water, and calcium carbonate, all the manganese is precipitated in the quadrivalent condition as manganite (*e.g.*, $ZnO.MnO_2$). The precipitate is then dissolved in an excess of ferrous ammonium sulphate solution and the excess of the latter is titrated with a standard potassium dichromate solution,

$$MnO_2+2FeSO_4+2H_2SO_4=Fe_2(SO_4)_3+MnSO_4+2H_2O.$$

SECTION III

Iodometry

Iodine dissolved in potassium iodide solution is also used as an oxidising agent. It oxidises a feebly alkaline solution of arsenious oxide to arsenic acid according to the following reactions :

$$As_2O_3+2I_2+2H_2O=As_2O_5+4HI.$$

or $$Na_3AsO_3+I_2+H_2O=Na_3AsO_4+2HI.$$

The ionic equation is :

$$AsO_3^{---}+I_2+H_2O\rightleftharpoons AsO_4^{---}+2H^++2I^-.$$

This reaction is reversible and so in order to make the reaction quantitative, the hydriodic acid must be removed from the field of action as soon as it is formed. This is accomplished by carrying on the reaction in presence of an excess of sodium bicarbonate.

No. 8

Titration of arsenious oxide with iodine

Suppose we are to determine exactly the strength of an arsenious oxide solution of given approximate strength (say $N/20$). This can be accomplished by titrating it against an iodine solution of approximately $N/20$ strength which in turn is standardised against an arsenious oxide solution of known strength (about $N/20$) which should be prepared.

(*i*) *Preparation of an arsenious oxide solution of known strength, about* $N/20$). The equivalent weight of As_2O_3 is 49·455, because one molecule is oxidised by four iodine atoms (equivalent weight will be $^1/_4$ of mol. wt. of. As_2O_3, *i.e.*, $\frac{197\cdot82}{4}=49\cdot455$)

Hence for preparing 100 ml. of $N/20$ solution, we require $\frac{49\cdot455}{20\times10}$ g. of $As_2O_3=0\cdot2473$ g.

Weigh out exactly about 0·2473 g. of As_2O_3 and dissolve it in about 2 ml. of shelf caustic soda solution(warm if necessary).

Now add 20 ml. of water. Add to it 2 drops of phenolphthalein solution and then dilute H_2SO_4 till the pink colour is discharged. Then add a saturated solution of sodium bicarbonate in excess and make up the solution to 100 ml. in the measuring flask with distilled water. Suppose, we have weighed *m g.* of As_2O_3; its strength will be

$$\frac{N \times 10 \times m}{49 \cdot 455} = \frac{Nm}{4 \cdot 9455}$$

(*ii*) *Preparation of about N/20 iodine solution*—The equivalent weight of iodine is 126·92; so that for $N/20$ solution, we require $\frac{126 \cdot 92}{20}$ g., *i.e.*, 6·346 g. of iodine per litre. Take this weight of iodine and add to it about 10 g. of pure potassium iodide and a few drops of water and stir well. When all iodine has gone to a homogeneous mass, add more water and further dilute it up to a litre. This is about $N/20$ iodine solution.

(*iii*) *Preparation of starch solution* (*to be used as indicator*)—Take a pinch of starch and make a paste of it with a few drops of cold water in a beaker. Add boiling water to this paste. This gives a starch solution which is used as indicator; it gives a blue colour with a dilute solution of iodine.

(*iv*) *Standardising the iodide solution with the prepared arsenious oxide solution*—Fill up the burette with iodine solution. Take 10 ml. of the prepared As_2O_3 solution in a clean beaker, add to it some saturated solution of (or even solid) sodium bicarbonate and some starch solution (about 10 drops). Run in iodine till a faint blue colour is just obtained. Repeat this till you get concordant values. Let v ml. of iodine be required for 10 ml. of As_2O_3 solution prepared.

$\therefore$ Strength of iodine solution $\times v_1$ ml. = Strength of As_2O_3 $\times$ 10 ml.

If N/x be the strength of the iodine solution; then

$$\therefore \qquad N/x = \frac{N \times m}{4 \cdot 9455} \times \frac{10}{v_1}.$$

(*v*) *Determination of the strength of a given As_2O_3 solution of an unknown strength*—Take 10 ml. of the given As_2O_3 solution in a clean beaker, add to it some saturated solution of sodium bicarbonate and about 10 drops of starch solution. Titrate with iodine as above. Let v_2 ml. of iodine be required for 10 ml. of the given unknown As_2O_3 solution.

Let the strength of the unknown solution be N/y.

$$\therefore \qquad N/y \times 10 = \text{Strength of iodine solution} \times v_2.$$

$$\therefore \qquad N/y = \frac{N \times m}{4 \cdot 945} \times \frac{10}{v_1} \times \frac{v_2}{10}$$

$$= \frac{N \times m}{4 \cdot 945} \times \frac{v_2}{v_1}$$

$$\text{Amount of } As_2O_3 \text{ per litre} = \frac{49 \cdot 45 \times m}{4 \cdot 945} \times \frac{v_2}{v_1} \text{ g.}$$

$$= 10m \times \frac{v_2}{v_1} \text{ g.}$$

Numerical—Find out the concentration in grams per litre of a given iodine solution, 12·5 ml. which were required for 10 ml. of an arsenious oxide solution (containing 0·1978 g. of the oxide in 100 ml. of the solution) in titration.

The equivalent weight of As_2O_3=49·45.

∴ The strength of As_2O_3 solution

$$= \frac{0 \cdot 1978 \times 10}{49 \cdot 45} = \frac{N}{25}$$

The strength of iodine solution $N/x \times$ vol.

$$= \text{the strength of } As_2O_3 \times \text{vol.}$$

or $\qquad N/x \times 12 \cdot 5 = N/25 \times 10.$

$$N/x = \frac{N \times 10}{25 \times 12 \cdot 5} = N/31 \cdot 25$$

Since the equivalent weight of iodine is 127, the strength of the iodine solution is 127/31·25 g. or 4·064 g. per litre.

No. 9

Titration of iodine with sodium thiosulphate

Sodium thiosulphate reacts with iodine giving sodium iodide and sodium tetrathionate :

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$
$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^-.$$

Of these solutions, only iodine is coloured and so it is possible to some extent to ascertain the end point by the disappearance of the faint yellow colour of dilute aqueous solution (in fact, the solution in KI) of iodine. But the end point is rendered much more obvious and accurate by adding starch solution which gives an intense blue colour in presence of traces of iodine. In strong iodine solutions, the colour with starch is dirty brown. Hence the titration

should be carried out as far as possible without starch (till the yellow colour becomes faint); the starch is added towards the end when about 4 or 5 drops of sodium thiosulphate solution further added would complete the titration.

Numerical—Find out the concentration of a hypo, $Na_2S_2O_3.5H_2O$, solution in grams per litre, 10 ml. of which just decolourised 15 ml. of $N/20$ iodine solution.

Strength of hypo solution $N/x \times$ vol.

$=$strength of iodine solution $\times$ vol.

$$N/x \times 10 = N/20 \times 15$$

$$\therefore \quad \frac{N}{x} = \frac{N}{20} \times \frac{15}{10} = N/13 \cdot 33$$

The equivalent weight of hypo is 248·2.

∴ the concentration of hypo solution is

$$248 \cdot 2/13 \cdot 33 \text{ g. per litre.}$$

$$= 18 \cdot 61 \text{ g. per litre.}$$

TITRATION OF THE LIBERATED IODINE

An advantage may be taken of the hypo–iodine reaction in determining the strength of $K_2Cr_2O_7$ or $CuSO_4$ solutions iodometrically. Potassium dichromate solution in presence of dilute H_2SO_4 (and copper sulphate without H_2SO_4) liberates iodine from potassium iodide and this liberated iodine is titrated against a solution of thiosulphate :

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 3I_2 + 7H_2O + 4K_2SO_4 + Cr_2(SO_4)_3.$$

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4.$$

The equations may be written in ionic forms :

$$Cr_2O_7^{--} + 14H^+ + 6I^- = 2Cr^{+++} + 7H_2O + 3I_2.$$

$$2Cu^{++} + 2I^- = 2Cu^+ + I_2.$$

The amount of iodine liberated from KI is proportional to the amount of $K_2Cr_2O_7$ or $CuSO_4$ present. The liberated iodine is titrated against hypo.

No. 10

Determination of the strength of a $K_2Cr_2O_7$ *solution using* KI *and sodium thiosulphate*—The reaction for this has already been explained. The process consists of the following steps:—

(i) *Preparation of a solution of* $K_2Cr_2O_7$ *of known strength* (about $N/20$)—Weigh out exactly about $49 \cdot 03/(20 \times 10) = 0 \cdot 2451$ g. of a good sample of $K_2Cr_2O_7$, dissolve it in water and make the solution up to 100 ml. in a measuring flask. Suppose you have weighed m g. of dichromate for 100 ml. of solution; the strength of the solution is

$$\frac{N.10m}{49 \cdot 03} = \frac{N.m}{4 \cdot 903}$$

(*ii*) *Preparation of sodium thiosulphate solution*—The equivalent weight of sodium thiosulphate, $Na_2S_2O_3.5H_2O$, is $248 \cdot 2$, so that for preparing a litre of $N/20$ solution, we require $248 \cdot 2/20 = 12 \cdot 410$ g. of the salt.

Weigh out about $12 \cdot 410$ g. of sodium thiosulphate, dissolve it in water and make the solution to about a litre. This gives about $N/10$ sodium thiosulphate solution.

(*iii*) *Preparation of potassium iodide solution*—Prepare about 10 per cent. solution of potassium iodide and take about 10 ml. of this solution for each titration.

(*iv*) *Preparation of starch solution*—This has already been described.

(*v*) *Standardising sodium thiosulphate solution with the prepared* $K_2Cr_2O_7$ *solution*—Fill up your burette with sodium thiosulphate solution. Take 10 ml. of the prepared $K_2Cr_2O_7$ solution in a clean beaker, and add to it about 10 ml. of dilute H_2SO_4 and about 10 ml. of potassium iodide solution. Titrate at once the liberated iodine with hypo till a faint yellow colour of iodine is left. Now add about 10 drops of starch solution, and complete the titration. Repeat the titration till you get concordant values.

Suppose v_1 ml. of sodium thiosulphate solution is required for 10 ml. of $K_2Cr_2O_7$ solution. Let the strength of the hypo solution be N/x.

$\therefore N/x \times v_1$ ml. = Strength of the prepared $K_2Cr_2O_7 \times 10$ ml.

Strength of the prepared $K_2Cr_2O_7 = \dfrac{N.m}{4 \cdot 903}$

$$\frac{N}{x} = \frac{N \times m}{4 \cdot 903} \times \frac{10}{v_1}.$$

(*vi*) *Determining the strength of the given* $K_2Cr_2O_7$ *solution*—Fill up the burette with sodium thiosulphate solution. Take 10 ml. of the given $K_2Cr_2O_7$ solution in a clean beaker; add to it about 10 ml. dilute H_2SO_4 and about 10 ml. of potassium iodide solution. Titrate the liberated iodine with hypo as above. Repeat till you get concordant values. Suppose v_2 ml. of sodium thio-

sulphate solution are required for 10 ml. of the unknown given $K_2Cr_2O_7$ solution, the strength of which is N/y.

$$N/y \times 10 = \text{Strength of hypo} \times v_2$$

$$= \frac{N \times m}{4 \cdot 903} \times \frac{10}{v_1} \times v_2$$

$$\therefore \quad \frac{N}{y} = \frac{N \times m \times 10 \times v_2}{4 \cdot 903 \times v_1 \times 10}$$

$$= \frac{N \times m}{4 \cdot 903} \times \frac{v_2}{v_1}.$$

If the amount of $K_2Cr_2O_7$ per litre is to be calculated, substitute 49·03 for N, and get the amount of $K_2Cr_2O_7$ per litre $= 10\ mv_2/v_1$ g. per litre.

Numerical—10 ml. of a potassium dichromate solution liberated iodine from potassium iodide solution. When the iodine was titrated against hypo solution ($N/25$), the titre value was 16 ml. Find out the concentration of dichromate solution in grams per litre.

$$10 \text{ ml. of } N/x\ K_2Cr_2O_7 \text{ solution} \equiv I_2 \text{ liberated}$$
$$\equiv 16 \text{ ml. of } N/25 \text{ hypo.}$$

$$\therefore \quad 10 \times N/x = 16 \times N/25.$$

$$\therefore \quad \frac{N}{x} = \frac{16 \times N}{10 \times 25} = \frac{N}{15 \cdot 62}.$$

Since the equivalent weight of $K_2Cr_2O_7$ is 49·03, the strength of the solution is 49·03/15·62 = 3·190 g. per litre.

No. 11

Determination of the strength of a copper sulphate solution (approximate strength $N/20$) using potassium iodide and sodium thiosulphate—Copper sulphate liberates iodine from KI and this liberated iodine is titrated against a hypo solution:

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

Or written ionically;

$$2Cu^{++} + 2I^- = 2Cu^+ + I_2$$

$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^-.$$

Two molecules of copper sulphate liberate two atoms of iodine Hence, the equivalent weight of copper sulphate, $CuSO_4.5H_2O$, is the same as its molecular weight, *i.e.*, 249·71.

Hence in order to prepare $N/20$ copper sulphate solution, we require $249 \cdot 71/20 \times 10$ g. of copper sulphate for 100 ml. solution.

(*i*) *Preparation of a known standard copper sulphate solution* (*of approximate strength* $N/20$).—Weigh out exactly about 1·248 g. of A. R. quality copper sulphate, dissolve it in water and make the solution up to 100 ml. in a measuring flask.

Suppose you have weighed m g. of copper sulphate, the strength of the solution is $N \times m/24.971$.

(*ii*) *Preparation of sodium thiosulphate solution*—This is done exactly in the same way as in the last case of $K_2Cr_2O_7$ titration.

(*iii*) *Preparation of potassium iodide solution*—As before.

(*iv*) *Preparation of starch solution*—As before.

(*v*) *Standardising sodium thiosulphate solution*—Fill up your burette with sodium thiosulphate solution. Take 10 ml. of copper sulphate solution in a clean flask and add to it about 10 ml. of potassium iodide solution. Titrate the liberated iodine with hypo till a light yellow colour of iodine is left. Now add about 10 drops of starch solution and complete the titration. Repeat till you get concordant values. Let v_1 ml. of hypo be required for 10 ml. of copper sulphate solution; and let the strength of hypo solution be N/x.

$$\therefore\ N/x \times v_1 \text{ ml.} = \text{Strength of } CuSO_4 \text{ prepared} \times 10 \text{ ml.}$$

$$= \frac{N \times m}{24 \cdot 971} \times 10$$

$$N/x = \frac{N \times m}{24 \cdot 971} \times \frac{10}{v_1}$$

(*vi*) *Determination of the strength of the given unknown copper sulphate solution*—Fill up the burette with the given copper sulphate solution in a clean beaker; add to it about 10 ml. of potassium iodide solution and titrate the liberated iodine with hypo. Repeat till you get concordant values.

Let v_2 ml. of sodium thiosulphate solution be required for 10 ml. of the unknown copper sulphate solution, the strength of which is N/y.

$$\therefore\quad N/y \times 10 \text{ ml.} = \text{Strength of hypo} \times v_2.$$

$$= \frac{N \times m}{24 \cdot 971} \times \frac{10}{v_1} \times v_2$$

$$\frac{N}{y}=\frac{N\times m\times 10\times v_2}{24{\cdot}971\times v_1\times 10}$$

$$=\frac{N\times m}{24{\cdot}971}\times\frac{v_2}{v_1}$$

If the amount of copper sulphate per litre has to be calculated, put 249·71 for N, and get the amount of copper sulphate per litre $=10mv_2/v_1$ g.

Numerical—How many grams of copper oxide would be obtained from 24 ml. of a copper sulphate solution, the same volume of the solution of which liberates so much iodine which when titrated against $N/25$ hypo solution gives 15 ml. as the titre value?

24 ml. of N/x copper sulphate solution

$\equiv$iodine liberated from KI

$\equiv$15 ml. of $N/25$ hypo

$$24\times N/x=15\times\frac{25}{N}$$

$$\frac{N}{x}=\frac{15}{24}\times\frac{N}{25}=\frac{N}{40}$$

Since 1 mol. of $CuSO_4\equiv$1 mol. of CuO and the molecular weight of copper sulphate is also its equivalent weight in iodometry, the molecular weight of CuO is the equivalent weight of CuO.

$\therefore$ the equivalent weight of CuO=79·57

$\therefore$ a litre of $N/40$ $CuSO_4$ solution would give

79·57/40 g. of CuO.

$\therefore$ 25 ml. of the copper sulphate solution would give $\frac{79{\cdot}57}{40}\times\frac{25}{1000}$ g. of CuO

=0·0497 g. of CuO.

OTHER APPLICATIONS OF IODOMETRY

ESTIMATIONS BY IODINE.—

(*i*) *Estimation of tin by iodine*—A stannous chloride solution can be titrated with a standard solution of iodine, using starch as indicator. The stannous salt is oxidised to stannic.

$$SnCl_2+2HCl+I_2=SnCl_4+2HI$$

or

$$Sn^{++}+I_2=Sn^{++++}+2I^-.$$

The metallic tin can also be estimated in a similar way. The metal is dissolved in hydrochloric acid (the solution is hastened by adding a few drops of chloroplatinic acid solution). Stannous chloride thus obtained is then titrated with iodine.

$$Sn \equiv SnCl_2 \equiv 2I \equiv 2Na_2S_2O_3.5H_2O$$
$$118{\cdot}7 \quad 189{\cdot}62 \quad 253{\cdot}84 \quad 466{\cdot}4$$

(*ii*) *Estimation of antimony by iodine*—This estimation is similar to the arsenious oxide estimation. Take anhydrous tartar emetic, 2 g., and dissolve in water. Add sodium bicarbonate in excess, and titrate with iodine, using starch as indicator.

The presence of tartrate is essential to prevent the precipitation of the metal.

$$Sb_2O_3+2I_2+2H_2O=Sb_2O_5+4HI.$$
$$2Sb \equiv 2K\ (SbO)\ C_4H_4O_6 \equiv Sb_2O_3 \equiv 4I$$
$$2\times121{\cdot}76 \quad 2\times324{\cdot}93 \quad 291{\cdot}52 \quad 4\times126{\cdot}92$$

(*iii*) *Estimation of hydrogen sulphide by iodine*—The hydrogen sulphide solution, if sufficiently dilute, can be estimated by iodine. If the sulphide solution is strong, dilute it with air free water. To a given volume of the solution, add in excess a standard solution of iodine. A part of the iodine solution will react with the sulphide and the excess is titrated with a standard solution of hypo, using starch as indicator.

$$H_2S+I_2=2HI+S$$
or
$$S^{=}+I_2=S+2I^-$$
$$H_2S \equiv 2I$$
$$34{\cdot}08 \quad 253{\cdot}8$$

(*iv*) *Estimation of sulphur dioxide or sulphite by iodine*—Sulphur dioxide with an iodine solution is oxidised to sulphuric acid as follows :

$$SO_2+I_2+2H_2O=H_2SO_4+2HI$$
or
$$SO_2+I_2+2H_2O=2H^++SO_4^{=}+2H^++2I^-.$$

Add the solution of sulphur dioxide to a slight excess of a standard solution of iodine, acidify with hydrochloric acid and stir. Titrate the excess of iodine (left unreacted) with a standard solution of hypo, using starch as indicator.

Note that the sulphur dioxide solution is to be added to the iodine solution and not *vice versa*, otherwise a different reaction takes place.

Similarly, a weighed quantity of a sulphite, to be estimated, is added to a known volume of an iodine solution, taken in excess and acidified with hydrochloric acid. The excess of iodine is titrated with the hypo solution.

$$SO_2 \equiv 2I$$
$$64{\cdot}36 \quad 253{\cdot}8.$$

ESTIMATION BY THE USE OF POTASSIUM IODIDE.

(*i*) *Estimation of chlorine*—To the dilute solution of chlorine, add an excess of potassium iodide solution. Iodine is liberated corresponding to the concentration of chlorine, and is titrated with hypo, using starch as indicator.

$$2KI + Cl_2 = 2KCl + I_2$$
$$Cl \equiv I$$
$$35{\cdot}46 \qquad 126{\cdot}92$$

(*ii*) *Estimation of available chlorine from bleaching powder*—Weigh out a quantity of bleaching powder, and make a suspension with water and transfer it to 100 ml. flask. Take 20 ml. of the suspension by a pipette and add it to an excess of potassium iodide solution. Acidify with acetic acid, and titrate the iodine liberated with a standard solution of hypo, using starch as indicator.

35·46 g. of chlorine are equivalent to 126·92 g. of iodine.

Numerical 1—Calculate the purity of a sample of pyrolusite from the following data: 0·750 g. of the powdered sample reacted with strong hydrochloric acid, and liberated chlorine. This in turn liberated iodine from a solution of potassium iodide. The iodine solution was raised to 250 ml. volume. 25ml. of the iodine solution required 20 ml. of $N/25$ hypo solution for titration.

The strength of iodine solution $N/x \times$ vol.

$=$the strength of hypo$\times$ vol.

$$\therefore \quad N/x \times 25 = N/25 \times 20$$

$$\therefore \quad N/x = \frac{N}{25} \times \frac{20}{25} = \frac{N}{31{\cdot}25}$$

Chlorine liberated

$=$iodine in 250 ml. of $N/31{\cdot}25$ solution

$$= \frac{126{\cdot}9}{31{\cdot}25} \times \frac{250}{1000} \text{ g. of iodine}$$

Since $MnO_2 \equiv 2I$,

$2 \times 126{\cdot}9$ g. of iodine $\equiv 86{\cdot}9$ g. of MnO_2

$$\frac{126\cdot 9}{31\cdot 25} \times \frac{250}{1000} \text{ g. of iodine } \equiv \frac{86\cdot 9 \times 126\cdot 9 \times 250}{2 \times 126\cdot 9 \times 31\cdot 25 \times 1000} \text{ g. of}$$

$MnO_2 = 0.3475$ g. of MnO_2.

$\therefore$ 0.750 g. of the sample contains $0{\cdot}3475$ g. of MnO_2,

$\therefore$ 100 g. of the sample contains $\dfrac{0\cdot 3475}{0\cdot 750} \times 100$ g.

$= 46.33\%$ of MnO_2.

Numerical 2—Calculate the percentage of chlorine available from a sample of bleaching powder from the following data: $1{\cdot}25$ g. of the bleaching powder were suspended in water to 100 ml. Of this suspension, 25 ml. reacted with potassium iodide, and the iodine liberated corresponded to $12{\cdot}5$ ml. of $N/25$ hypo solution in titration.

N/x strength of bleaching powder solution $\times$ vol.

$\equiv$ iodine liberated

$\equiv$ strength of hypo solution $\times$ vol.

$N/x \times 25 = N/25 \times 12{\cdot}5$

$$N/x = \frac{N}{25} \times \frac{12\cdot 5}{25} = \frac{N}{50}.$$

Since $N/50$ of hypo $\equiv N/50$ of iodine $= N/50$ of chlorine and the equivalent weight of chlorine is $35{\cdot}46$, the bleaching powder contains $35{\cdot}46/50$ g. of chlorine per litre or $3{\cdot}546/50$ g. per 100 ml. of the suspension. This much of chlorine is present in $1{\cdot}25$ g. of the sample. Hence 100 g. of the sample contain

$$\frac{3\cdot 546}{50} \times \frac{100}{1\cdot 25} \text{ g. of chlorine} = 5\cdot 67\%.$$

(*iii*) *Estimation of bromine*—A dilute solution of bromine liberates iodine from a solution of potassium iodide; the iodine liberated is titrated with hypo solution using starch as indicator.

$$2KI + Br_2 = 2KBr + I_2$$

$$\underset{79\cdot 92}{Br} \equiv \underset{126\cdot 92}{I}$$

(*iv*) *Estimation of manganese dioxide in a sample of pyrolusite*—When manganese dioxide is heated with an excess of concentrated hydro-

chloric acid, chlorine is evolved equivalent to the "available" oxygen. The gas is passed into an excess of potassium iodide solution. The liberated iodine is then titrated with a standard solution of hypo.

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$$

$$2KI+Cl_2=2KCl+I_2$$

$$\underset{86\cdot9}{MnO_2} \equiv \underset{70\cdot91}{2Cl} \equiv \underset{16}{O} \equiv \underset{253\cdot8.}{2I.}$$

(*v*) *Estimation of chlorate, bromate and iodate*— (*a*) A chlorate when distilled with concentrated hydrochloric acid yields chlorine, which when passed through a solution of potassium iodide will liberate iodine. This may be titrated with hypo solution.

$$KClO_3+6HCl=KCl+3H_2O+3Cl_2.$$

$$\underset{122\cdot56}{KClO_3} \equiv \underset{83\cdot46}{ClO_3} \equiv \underset{212\cdot76}{6\ Cl} \equiv \underset{761\cdot52.}{6I}$$

(*b*) To a solution of bromate, add a considerable excess of solid potassium iodine, and add a large volume of concentrated hydrochloric acid. Wait for a few minutes and then titrate the liberated iodine with a solution of hypo.

$$KBrO_3+6KI+6HCl=KBr+6KCl+3H_2O+3I_2.$$

127·92 of BrO_3 radical correspond to 761·52 g. of iodine.

(*c*) The reaction with an iodate is instantaneous. To a solution of an iodate, add potassium iodide in excess and acidify with HCl : iodine is liberated, which is titrated with hypo.

$$KIO_3+5KI+6HCl=6KCl+3H_2O+3I_2.$$

174·92 g. of IO_3 radical correspond to 761·52 g. of iodine.

(*iv*) *Estimation of hydrogen peroxide*—A dilute solution of hydrogen peroxide (not more than 5 g. per litre) is added to a solution containing dilute sulphuric acid and potassium iodide; iodine is set free, and is titrated with a solution of hypo.

$$H_2O_2+2KI+H_2SO_4=K_2SO_4+2H_2O+I_2.$$

17 g. of hydrogen peroxide correspond to 126·92 g. of iodine.

SECTON IV
PRECIPITATION

Precipitation processess of volumetric analysis are based upon the formation of insoluble precipitates when the reacting solutions are brought together. Thus when a solution of silver nitrate is treated with a solution of sodium chloride or potassium thiocyanate, we get a white precipitate of silver chloride or silver thiocyanate:

$$AgNO_3 + NaCl = AgCl \downarrow + NaNO_3.$$

$$AgNO_3 + KCNS = AgCNS \downarrow + KNO_3.$$

These equations may be written in ionic forms:

$$Ag^+ + Cl^- = AgCl \downarrow.$$

$$Ag^+ + CNS^- = AgCNS \downarrow.$$

Hence, the amount of silver present in a solution may be estimated volumetrically by precipitating it as chloride or thiocyanate. Both of these precipitates are white and it is not convenient to ascertain the end point without an indicator. In the first case, a neutral solution of potassium chromate is used as indicator (*Mohr's method*); and in the second, an acidic solution of ferric alum. An excess of $AgNO_3$ over that required for NaCl will give a red colour with K_2CrO_4. In the second case, an excess of KCNS over that required for $AgNO_3$ will give a red colour with ferric alum (*Volhard's method*).

As one molecule of $AgNO_3$ reacts with one molecule of NaCl and also with one molecule of KCNS, the equivalent weights of $AgNO_3$ and KCNS will all be the same as their molecular weights.

No. 9

Mohr titration

Determination of the strength of a sodium chloride solution (of approximate strength N/20)—The process consists of the following operations:—

(*i*) *Preparation of a NaCl solution of known strength (app. N/20)*.—Equivalent weight of NaCl is 58·45. Hence for 100 ml. of *N*/20 solution, we require $58 \cdot 45/(20 \times 10)$ g. $= 0 \cdot 2923$ g.

Weigh out accurately about 0·2923 g. of pure A. R. quality NaCl, dissolve it in water and make the solution up to 100 ml. in a measuring flask. Suppose you have weighed *m* g. of NaCl; the strength of the solution will be $Nm/5 \cdot 845$.

(*ii*) *Preparation of about N/20 silver nitrate solution*—The equivalent weight of $AgNO_3$ is 169·9 and so *N*/20 solution contains 8·495 g. of $AgNO_3$ per litre. Hence weigh out about 8·495 g. of pure $AgNO_3$ and dissolve it in water and make it up to about a litre. This is approximately *N*/20 $AgNO_3$ solution.

(*iii*) *Standardising $AgNO_3$ solution against the prepared NaCl*—Take $AgNO_3$ solution in the burette. Now take 10 ml. of the prepared NaCl solution in a clean beaker and add to it a few drops of neutral K_2CrO_4 solution. Run in $AgNO_3$ solution from the burette till a red colour appears. Repeat the process till you get concordant values. Let v_1 ml. of $AgNO_3$ be required for 10 ml. of NaCl solution, and let the strength of $AgNO_3$ solution be N/x.

$\therefore$ $N/x \times v_1$ ml. = Strength of NaCl prepared $\times$ 10 ml.

$$\frac{N}{x} = \frac{N}{5{\cdot}845} \times m \times \frac{10}{v_1}.$$

(*iv*) *Determining the strength of the given unknown NaCl solution*—Fill up the burette with the standardised $AgNO_3$ solution. Take 10 ml. of the given unknown NaCl solution in a clean beaker, add to it a few drops of neutral K_2CrO_4 solution, and titrate against $AgNO_3$ solution as above.

Let the strength of the unknown solution of NaCl be N/y.

$$N/y \times 10 \text{ ml.} = \text{strength of } AgNO_3 \times v_2$$

$$= \frac{N \times m \times 10 \times v_2}{5 \cdot 845 \times v_1}$$

$$N/y = \frac{N \times m}{5 \cdot 845} \times \frac{10}{v_1} \times \frac{v_2}{10} = \frac{N \times m}{5 \cdot 845} \times \frac{v_2}{v_1}$$

If the amount of NaCl per litre has to be calculated, put 58·45 for N and get the amount of NaCl in grams per litre.

$$\therefore \text{ Strength of NaCl solution} = \frac{10m.v_2}{v_1}.$$

No. 12

Adsorption indicator method

Determination of the strength of a given silver nitrate solution against a standard solution of potassium chloride, using fluorescein (or dichlorofluorescein) as indicator.

Pipette out 10 ml. of the standard ($N/20$) solution of potassium chloride into a beaker. Add 10 drops of fluorescein indicator; and titrate with the given silver nitrate solution (taken in burette) in diffused light, while rotating the beaker constantly. At the close of the end point, the silver chloride coagulates appreciably, and the local development of a pink colour upon the addition of a drop of the silver nitrate becomes more and more pronounced. Continue the addition of the silver nitrate solution until the precipitate suddenly assumes a pronounced pink or red colour.

The calculations are as in 9 (*ii*) [For the reverse titration, *i.e.*, the chloride taken in burette and silver nitrate in beaker, tartrazine (4 drops of a 0·2 per cent solution per 100 ml.) is a suitable indicator. Near the end point, the almost colourless liquid assumes a blue colour.]

Indicators—(*i*) *Fluorescein*—Dissolve 0·1 g. of fluorescein in 100 ml. of 70 per cent. alcohol (or dissolve 0.1 g. sodium fluoresceinate in 100 ml. of water).

(*ii*) *Dichlorofluorescein*—Dissolve 0.1 g. of this indicator in 100 ml. of 60-70 per cent alcohol (or dissolve 0.1 g. of this Na-salt in 100 ml. of water).

No. 13

Volhard titration

Determination of the strength of a given silver nitrate (*of approximate strength* $N/20$)—This process consists of the following operations:

(*i*) *Preparation of a silver nitrate solution of unknown strength*(app. $N/20$). $N/20$ solution of $AgNO_3$ contains 8·495 g. of $AgNO_3$ per litre. Hence in order to prepare 100 ml. of the solution, weigh out exactly about 0·8495 g. of A. R. quality $AgNO_3$, dissolve it in water and make it up to 100 ml. Suppose you have weighed m g. of silver nitrate, the strength of the solution is $N\times 10m/169{\cdot}9 = N\times m/16{\cdot}99$.

(*ii*) *Preparation of about $N/20$ KCNS solution*—The equivalent weight of KCNS in 97·2 and so its $N/20$ solution contains 4·86 g. of KCNS per litre. Hence weigh out about 4·86 g. of KCNS, dissolve it in water and make it up to about a litre.

(*iii*) *Preparation of indicator*—This is prepared by boiling a saturated solution of ferric alum with a small amount of nitric acid until nitrous fumes have been expelled.

(*iv*) *Standardising KCNS solution against the prepared $AgNO_3$ solution*—Fill up the burette with KCNS solution. Take 10 ml. of the prepared $AgNO_3$ solution in a clean beaker; add about 0·5 ml. of the indicator and run in KCNS solution till a faint blood red colour is obtained. Repeat the process till you get concordant values. Let this be v ml. and let the strength of KCNS solution be N/x.

$$N/x \times v_1 \text{ ml.} = \text{Strength of } AgNO_3 \text{ prepared} \times 10 \text{ ml.}$$

$$N/x = \frac{N}{16{\cdot}99} \times m \times \frac{10}{v_1}$$

(*v*) *Determination of the strength of given unknown $AgNO_3$ solution*—Fill up the burette with the standardised KCNS solution. Take

10 ml. of the given unknown $AgNO_3$ solution in a clean beaker; add to it about 2 ml. of the indicator solution and titrate as above. Repeat till you get concordant values. Let this be v_2 ml. and let the strength of the unknown silver nitrate solution be N/y

$$\therefore \quad N/y \times 10 \text{ ml.} = \text{Strength of KCNS} \times v_2.$$

$$\therefore \quad N/y = \frac{N \times m}{16 \cdot 99} \times \frac{10}{v_1} \times \frac{v_2}{10} = \frac{N \times m}{16 \cdot 99} \times \frac{v_2}{v_1}.$$

If the amount of $AgNO_3$ per litre has to be calculated, put 169·9 for N and get the amount of $AgNO_3$ per litre in the given solution.

The strength of the given silver nitrate solution is

$$= \frac{169 \cdot 9 \times m}{16 \cdot 99} \times \frac{v_2}{v_1} = 10m. \frac{v_2}{v_1} \text{ g. per litre.}$$

Numerical—1. Find out the strength in grams per litre of a potassium chloride solution which for its 10 ml. required 15 ml. of $N/25$ silver nitrate solution for titration.

Strength of KCl solution, $N/x \times$ vol.

$$= \text{Strength of } AgNO_3 \times \text{vol.}$$

$$\therefore \quad N/x \times 10 = N/25 \times 15.$$

$$\therefore \quad \frac{N}{x} = \frac{N}{25} \times \frac{15}{10} = \frac{N}{16 \cdot 66.}$$

Since the equivalent weight of KCl is 74·46, the strength of KCl solution is

$$74 \cdot 46/16 \cdot 66 \text{ g.} = 4 \cdot 4676 \text{ g. per litre.}$$

2. Find out the strength of a potassium thiocyanate solution in grams per litre, 20 ml. of which require 24 ml. of $N/24$ silver nitrate solution.

Strength of KCNS, $N/x \times$ vol.

$$= \text{Strength of } AgNO_3 \times \text{vol}$$

$$\therefore \quad \frac{N}{x} \times 20 = \frac{N}{24} \times 24$$

$$\therefore \quad N/x = \frac{N \times 24}{24 \times 20} = N/20$$

Since the equivalent weight of KCNS is 97·17, the strength of the solution is 97·17/20 g. or 4·858 g. per litre.

No. 14

Adsorption titrations of bromides and iodides

Determination of the strength of silver nitrate solution against a standard solution of potassium bromide using eosin as indicator.

Weigh out accurately the requisite quantity of potassium bromide so as to give 100 ml. of a standard *N*/20 solution, and dissolve it in water and raise to 100 ml. volume in the measuring flask. Pipette out 10 ml. of this solution in a beaker (or a small conical flask) and add 30 ml. of water and a few ml. of 6 *N* acetic acid and 10 drops of eosin indicator. Titrate it against the given solution of silver nitrate with constant agitation in a diffuse light. The silver bromide flocculates a little before the end point, and the local development of the red colour becomes more and more pronounced upon the addition of silver nitrate solution. Continue adding drops from the burette with vigorous swirling of the liquid, until the precipitate suddenly assumes a pronounced magenta colour.

1 ml. of *N* $AgNO_3 \equiv 0 \cdot 07992$ g. of $Br \equiv 0 \cdot 1190$ g. of KBr.

Eosin indicator—Dissolve 0·1 g. of eosin in 100 ml. of 70 per cent alcohol (or 0·1 g. of its Na-salt in 100 ml. of water).

For iodide estimations—The indicator used is di-iodo di-methyl-fluorescein (1 g. in 100 ml. of 70 per cent. alcohol.).

Near the end point, flocculation of silver iodide occurs and the colour change is from orange-red to blue-red.

Numerical Questions

A

1. 2 grams of a sample of Mohr's salt (ferrous ammonium sulphate), when estimated yielded 0·3 g. of Fe_2O_3 : Find out the percentage purity of the sample. How many ml. of *N*/10 $KMnO_4$ would be required to oxidise 0·15 g. of the above sample

(*Ans.* 73·65%; 2·82 ml.)

2. A copper sulphate solution yielded 0·25 g. of cupric oxide when estimated gravimetrically. How many grams of iodine will it liberate from potassium iodide solution? (*Ans.* 399 g.)

3. A solution of ferrous sulphate taken 20 ml. was titrated against *N*/20 $K_2Cr_2O_7$ solution. The titre value was 16 ml. Calculate the strength of ferrous sulphate, $FeSO_4 . 7H_2O$ in grams per litre in the solution (*Ans.* 11·12 g.)

How many grams of Fe_2O_3 will be obtained if 50 ml. of the above solution are taken for estimation? (*Ans.* 0·1957 g.)

4. A solution of pure copper sulphate, $CuSO_4.5H_2O$, taken 25 ml. was estimated for SO_4. It gave 0·2580 g. of $BaSO_4$ precipitate. Find out the strength of the solution in terms of grams CuO per litre and in terms of grams $CuSO_4.5H_2O$ per litre. (*Ans.* 3·52 g.; 11·04 g.).

5. How many grams of caustic soda would be necessary to precipitate copper completely as oxide from 50 ml. of a copper sulphate solution, the strength of which is *N*/5 with respect to iodine, when estimated iodometrically? (*Ans.* 0·8 g.)

6. A solution of silver nitrate, taken 25 ml. yields 0·2867 g. AgCl. Calculate its strength in normality, and in grams of silver nitrate per litre. (*Ans.* *N*/12·49; 13·6 g.).

7. How many ml. of *N*/20 KCl would be necessary to precipitate silver completely from 25 ml. of silver nitrate solution of *N*/15 strength ? (*Ans.* 33·33 ml.).

8. A solution of silver nitrate, taken 20 ml. gave 0·43 g. of silver chloride. How many ml. of *N*/24 KCNS would be necessary for titrating 5 ml. of the above $AgNO_3$ solution? (*Ans.* 18·75 ml.)

9. How many grams of $BaSO_4$ precipitate will be obtained from 25 ml. of *N*/20 ferrous ammonium sulphate? (*Ans.* 0·5834 g.)

10. A solution, 25 ml. in volume, is a mixture of hydrochloric and sulphuric acids. When estimated gravimetrically, it gave 0·1433 g. of silver chloride, and 0·2334 g. of barium sulphate. Find out the strength of the acids separately in the mixture. What will be the total strength of the acidity in terms of normality (*Ans.* *N*/25 HCl; *N*/12·5 H_2SO_4; total acidity *N*/8·33).

11. 5 g. of potassium sulphate were dissolved in 250 ml. of volume. How many ml. of the solution be taken as to yield 1·2 g. of barium sulphate precipitate? (*Ans.* 44·78 ml.).

12. 25 ml. of a solution of copper sulphate, when added to a potassium iodide solution, yielded iodine which required 50 ml. of *N*/10 hypo solution. Find out the amount of copper sulphate, $CuSO_4.5H_2O$, dissolved per litre. (*Ans.* 49·942 g.).

How much barium sulphate would be obtained from 50 ml. of the above copper sulphate solution, if precipitated with barium chloride ? (*Ans.* 2·3342 g.).

13. 20 ml. of a solution of $ZnSO_4.7H_2O$, containing 28.75 g. of the salt per 100 ml., were estimated gravimetrically, both for zinc and sulphate ions. How much ZnO and $BaSO_4$ would be obtained? (*Ans.* ZnO 1·6276 g.; $BaSO_4$. 4·6684 g.).

14. How many grams of metallic zinc would you dissolve per litre in sulphuric acid as to yield a solution, 25 ml. of which may give 0·4095 g. of zinc oxide precipitate? (*Ans.* 13.076 g.).

15. How many grams of potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3$-$24H_2O$, be taken as to yield 0.2038 g. of Al_2O_3 ? (*Ans.* 1.8975 g.).

16. A sample of alum has 80% purity; how many grams of Al_2O_3 would be obtained from its 2 grams of anhydrous mass? (*Ans.* 0·4932 g.).

17. 5 grams of aluminium were dissolved to 200 ml. solution Find out the amount of Al_2O_3 obtained from 25 ml. of its solution. (*Ans.* 1·18 g.).

18. How much pure calcium oxide, CaO, be dissolved per litre in HCl as to yield per 20 ml. of solution 0.3202 g. of dry calcium oxalate? How much will calcium carbonate be obtained from this amount of calcium oxalate on careful ignition. (*Ans.* 7·01, 0·2502 g.).

19. Calculate the amount of (*i*) MgO and (*ii*) $Mg_2P_2O_7$ corresponding to 20 ml. of solution, containing 12·16 g. of magnesium metal per litre. (*Ans.* (*i*) 0·4032 g; (*ii*) 1·1134 g.).

20. Calculate the purity of a magnesium sulphate, $MgSO_4 \cdot 7H_2O$, sample, 2 grams of which yield 0·8 g. of $Mg_2P_2O_7$. (*Ans.* 88·5%).

B

21. A solution contains 5·3. g. of sodium carbonate and 8 g. of caustic soda per litre. The mixture, of which 20 ml. have been taken, is titrated with *N*/10 hydrochloric acid. What will be the titre readings if (*i*) methyl orange be taken as indicator from the very beginning; (*ii*) and if phenolphthalein be taken as an indicator from the beginning. (*Ans.* (*i*) 60 ml., (*ii*) 50 ml.).

22. 50 ml. of a solution containing sodium carbonate and sodium hydroxide were neutralised by 43·2 ml. of *N* HCl (methyl orange, used as indicator). The carbonate was precipitated as $CaCO_3$ by $CaCl_2$, and filtered off. The sodium hydroxide, after precipitation of the carbonate, was found to be neutralised by 20·8 ml. of *N* HCl (using phenolphthalein). Find out the concentration in grams per litre of caustic soda and sodium carbonate in solution. (*Ans.* NaOH 16.64 g.; Na_2CO_3 23·74 g.).

23. A solution contained a mixture of sodium carbonate and sodium bicarbonate. 50 ml. of the solution were titrated with *N* HCl. At first, phenolphthalein was used and an end point was obtained with 30 ml. of HCl. At this stage, methyl orange was introduced, and the titration completed on a further addition of 50 ml. of HCl. Find out the concentration of carbonate, Na_2CO_3, and bicarbonate, $NaHCO_3$, in grams per litre. (*Ans.* 63·6 g. Na_2CO_3; 33·6 g. $NaHCO_3$).

24. A mixture contained in a litre 20 g. of caustic soda, 20 g. of sodium bicarbonate and 20 g. of sodium carbonate. What will be the titre values if (*i*) first titrated with phenolphthalein; (*ii*) methyl orange added after the first end point, and (*iii*) if methyl orange used from the very beginning;—the acid used for titration is $\mathcal{N}$ HCl, and 50 ml. of the mixture titrated each time. (*Ans.* (*i*) 34·4 ml. (*ii*) 21·3 ml., (*iii*) 55·7 ml.).

C

25. 1·147 g. of pure iron were dissolved in acid and raised up to 250 ml. 25 ml. of this ferrous solution, when titrated with a $K_2Cr_2O_7$ solution, required 21.1 ml. Find out the strength of $K_2Cr_2O_7$ solution in grams per litre. (*Ans.* 4·647 g.).

26. Calcium from a solution was precipitated as calcium oxalate, and the oxalate was filtered, washed and redissolved in acid, and raised to 250 ml.; 25 ml. of this solution, when titrated with $\mathcal{N}/20$ $KMnO_4$, required 30 ml. for oxidation. Find out the total weight of calcium in the solution. (*Ans.* 0·3006 g.).

$$5Ca \equiv 5H_2C_2O_4 \equiv 2KMnO_4 \equiv 5O \equiv 10H.$$

27. What is the weight in grams of available oxygen per litre from a solution of hydrogen peroxide, 10 ml. of which when titrated with $\mathcal{N}/10$ $KMnO_4$ solution, required 25 ml. for the reaction.

$$2KMnO_4+5H_2O_2+4H_2SO_4=5O_2+8H_2O+2KHSO_4+MnSO_4$$

(*Ans.* 2 g.).

28. What is the concentration of a solution of sodium nitrite, $NaNO_2$, in grams per litre, 10 ml. of which when titrated with $\mathcal{N}/20$ $KMnO_4$, in presence of dilute sulphuric acid at 40°, required 30 ml. for oxidation. The reaction is:

$$2KMnO_4+5HNO_2+3H_2SO_4=K_2SO_4+2MnSO_4+5HNO_3+3H_2O.$$

? (*Ans.* 5·175 g.).

29. How will you estimate the percentage of oxalate radical C_2O_4'', in a given sample of the salt? How much per cent oxalate is in a pure sample of oxalic acid, $H_2C_2O_4 . 2H_2O$? (*Ans.* 69·84 per cent).

0.5 gram of an oxalate was dissolved and the solution raised to 40 ml. and 10 ml. of the solution titrated with $\mathcal{N}/20$ $KMnO_4$. The titration required 15 ml. of $KMnO_4$. Find out the percentage of oxalate in the sample(*Ans.* 66 per cent).

30. A ferrous sulphate sample had 80 per cent purity 0·2 grams of the salt, $FeSO_4 . 7H_2O$, were dissolved and raised to 100 ml. How many ml. of $\mathcal{N}/20$ $KMnO_4$ would be necessary to titrate 10 ml. of the ferrous solution? (*Ans.* 11·5 ml.).

D

31. Find out the purity of hypo sample, $Na_2S_2O_3.5H_2O$, of which 30 g. were dissolved in a litre; 20 ml. of the solution when titrated with $N/20$ iodine solution required 15 ml. (*Ans.* 62·05 per cent).

32. How many grams of iodine be taken per litre, so that 10 ml. of the solution may require 15 ml. of $N/10$ As_2O_3 in titration? (*Ans.* 9·519 g.).

33. 10 ml. of a solution of $KMnO_4$, added to KI solution, liberated iodine, corresponding to 8·6 ml. of $N/20$ hypo solution. Find out the strength of $KMnO_4$ solution in grams per litre. (*Ans.* 1·359 g.).

34. How many grams of iodine will be liberated from KI solution by a copper sulphate solution which gives 0·4 gram of CuO on precipitation with alkali ? (*Ans.* 0·638 g.).

35. 10 ml. of a solution of potassium dichromate liberated iodine from KI, which required 12 ml. of $N/20$ hypo solution for titration. Find out the strength of $K_2Cr_2O_7$ solution in grams per litre. (*Ans.* 2.9418 g.).

36. How many grams of ferric oxide, Fe_2O_3, would be obtained from 50 ml. of a solution of ferric chloride of which 10 ml. when titrated iodometrically require 8 ml. of $N/20$ hypo solution, the reaction is:

$$2FeCl_3+2KI=2FeCl_2+2KCl+I_2.$$

(*Ans.* 0.1597 g.).

37. 10 grams of a bleaching powder sample were dissolved to 250 ml. solution. 25 ml. of the solution were added to KI solution taken in excess and acidified with acetic acid. The iodine liberated was titrated with $N/2$ hypo solution. If the available chlorine is 30 per cent., find out in ml. the hypo solution required.

$$CaOCl_2 \equiv Cl_2 \equiv 2I.$$

(*Ans.* 17·03 ml.).

38. A sample of pyrolusite weighed 2 grams. The sample contains 60 per cent of pure MnO_2. It was heated with strong HCl, and the chlorine liberated was passed through a KI solution. The iodine solution was diluted to 200 ml. How many ml. of $N/20$ hypo would be required to react with 10 ml. of this diluted iodine solution.

$$MnO_2+4HCl=MnCl_2+Cl_2+2H_2O.$$

$$MnO_2 \equiv Cl_2 \equiv 2I.$$

(*Ans.* 22·7 ml.)

39. How would you prepare and standardise an $N/10$ solution of silver nitrate?

0·22 g. of a mixture of NaCl and KCl were titrated with 0·922 $N/10$ solution of $AgNO_3$, and required 33 ml. for complete reaction. What are the percentages of NaCl and KCl in the mixture?

(*Ans.* NaCl 39·6 per cent, KCl 60·4 per cent.).

40. 1·137 g. of pure iron were dissolved in an acid and raised to 250 ml.; 25 ml. of this ferrous solution when titrated with a $K_2Cr_2O_7$ solution, required 21.1 ml. of the dichromate solution. Find out the strength of the dichromate solution in grams per litre. (*Agra. Univ.*, *B.Sc.*, 1945). (*Ans.* 4·73 g.).

41. 0·261 g. of a sample of pyrolusite was heated with an excess of HCl and the chlorine evolved was passed into a solution of KI. The liberated iodine required 90 ml. of $N/30$ hypo. Calculate the percentage of pure MnO_2 present in the ore. (*Agra Univ.*, *B.Sc.*, 1942). (*Ans.* 50%).

42. How many grams of iodine will be liberated from a strong solution of KI when 100 ml. of copper sulphate solution containing 24·96 g. of the crystalline salt ($CuSO_4.5H_2O$) per litre are added to it? Give full equations of the reaction. (*Agra Univ.*, *B.Sc.*, 1944). *Ans.* 1·2692 g.).

43. Calculate in grams per litre the amount of ferrous and ferric iron present in a solution containing both from the following data:

25 ml. of the iron solution required for titration 24 ml. of the standard $KMnO_4$ solution. 100 ml. of the same solution were reduced completely with zinc and sulphuric acid, and the reduced solution was diluted to 250 ml.; 50 ml. of this dilute solution required 36·75 ml. of the same $KMnO_4$ solution.

The solution of $KMnO_4$ was titrated against $N/10$ oxalic acid and it was found that 25 ml. of $N/10$ oxalic acid were equivalent to 37·5 ml. of $KMnO_4$. (*B. H. U.*, *B. Sc.*, 1936). (*Ans.* Ferrous 3·57 g., ferric 3·266 g.).

44. How is a decinormal solution of "hypo" prepared?

100 ml. of a solution of NaCl and copper sulphate gave 1·434 g. of AgCl in a quantitative experiment. Another 100 ml. of the same solution on the addition of an excess of KI consumed 100 ml. of $N/10$ hypo. Find the amounts of NaCl and crystallised copper sulphate $CuSO_4$. $5H_2O$, in grams per litre. (*Alld. Univ.*, *B.Sc.*, 1957). (*Ans.* NaCl 5·845 g.; copper sulphate 24·97 g.).

45. One gram of pyrolusite is treated with an excess of concentrated HCl and the chlorine evolved is passed through KI solution in bulbs. This solution together with the liberated iodine, is diluted to 250 ml. and on titration with $N/50$ $Na_2S_2O_3$ solution, 25 ml. of the former are found equivalent to 31 ml. of the latter. Calculate the percentage of MnO_2 in the mineral. (*Alld. Univ., B. Sc.*, 1935). (*Ans.* 26·24 per cent).

46. 0.2 g. of a sample of pyrolusite, when warmed with excess of hydrochloric acid, and the evolved chlorine passed into excess of potassium iodide solution, required for the liberated iodine 30 ml. of $N/10$ thiosulphate solution. What is the percentage of pure manganese dioxide? (*Agra Univ., B.Sc.*, 1932. (*Ans.* 30·10 per cent).

47. Indicate the use of sodium thiosulphate in analytical chemistry.

0·2915 g. of a manganese ore was heated with hydrochloric acid and the chlorine evolved was passed into a solution of potassium iodide. The liberated iodine required 20.5 ml. of $0 \cdot 1N$ sodium thiosulphate solution. Calculate the percentage of manganese dioxide in the ore. (*Agra Univ., B. Sc.*, 1935). (*Ans.* 13·3 per cent.)

48. Explain fully, with equations, the reactions underlying the analytical process in the titration of iron with permanganate and dichromate. (*Alld. Univ., B. Sc.*, 1945).

49. A quantity of $KMnO_4$ was boiled with hydrochloric acid and the gas evolved was led into a solution of KI. When the reaction was complete, the iodine liberated was titrated with a solution of sodium thiosulphate containing 124 g. of $Na_2 S_2 O_3 . 5H_2O$ per litre. It was found that exactly 60 ml. were required to decolourise the solutions of iodine. What weight of $KMnO_4$ was used? (*Agra Univ. B.Sc.*, 1947). (*Ans.* 0.9486 g.).

50. 0·6 of a sample of pyrolusite was boiled with 210 ml. of decinormal oxalic acid and excess of dilute sulphuric acid. The liquid was then filtered and the residue washed. The filtrate and washings were then mixed and made up to 500 ml. in a measuring flask. 100 ml. of this solution required 50 ml. of $N/30$ $KMnO_4$ solution. Calculate the percentage of MnO_2 in the given sample. (*Agra Univ., B. Sc.*, 1946; *Alld. Univ., B. Sc., II*, 1957). (*Ans.* 84·58%).

51. 1.137 g. of pure iron were dissolved in an acid and raised to 250 ml.; 25 ml. of this ferrous solution when titrated with $K_2Cr_2O_7$ solution required 21·1 ml. of the dichromate solution. Find out the strength of the dichromate solution in grams per litre. (*Agra Univ., B.Sc.*, 1945). (*Ans.* 9·46 g.).

52. Calculate the number of ml. of potassium dichromate solution containing 4·9 g. per litre of the salt required to oxidise 0·5 g. of iron dissolved in dilute sulphuric acid. In an actual experiment, 88·5 ml. were required. How do you account for the difference? (*Agra Univ., B. Sc.* 1948). (*Ans.* 89.3 ml.)

53. 0·2828 g. of iron wire was dissolved in excess of dilute sulphuric acid and the solution made up to 100 ml.; 20 ml. of this solution required 30 ml. of *N*/30 potassium dichromate solution for exact oxidation. Calculate the percentage purity of the wire. (*Agra Univ., B Sc.*, 1949). (*Ans.* 99%).

54. 0.5 g. of a sample of a bleaching powder was suspended in water and excess of KI added. On acidifying with dilute sulphuric acid, iodine was liberated which required 50 ml. of *N*/10 $Na_2S_2O_3 \cdot 5H_2O$ solution. Calculate the percentage of available chlorine in the bleaching powder. Give equations. (*Agra Univ., B. Sc.*, 1950). (*Ans.* 35·50%).

55. How can a standard solution of copper sulphate be prepared? How would you proceed to determine the percentage purity of a given copper sulphate sample (*a*) gravimetrically, and (*b*) volumetrically. (*Alld. Univ., B. Sc. II*, 1957).

PART VII

Organic Substances and their Indentification

SECTION I

DETECTION OF ELEMENTS IN ORGANIC COMPOUNDS

Detection of Carbon and Hydrogen. All organic compounds contain carbon, and it is usually not necessary to detect carbon in them, unless one intends distinguishing them from inorganic. (i) Most organic substances char when strongly heated. They can be taken on a metallic spatula or on the blade of a knife and tested. (ii) Some of them blacken when heated with concentrated sulphuric acid. (iii) In case of those substances which do not answer these tests, they may be dried, powdered, and mixed with seven times their weight of powdered dry *copper oxide*, and strongly heated. This may be done in a dry test tube, fitted with cork and a delivery tube. The tube is clamped horizontally and heated. The gases evolved are allowed to bubble through lime water. If the latter is rendered turbid, the presence of carbon is established.

The formation of water drops on the cooler sides of the test tube indicates the presence of *hydrogen* in the compound. If the upper portions of the tube are dusted with anhydrous copper sulphate the presence of even traces of moisture can be detected by the blue colour, which copper sulphate assumes after absorbing moisture.

Detection of Nitrogen— (*i*) Some of the compounds, evolve ammonia, when strongly heated with soda-lime in a hard glass test tube, in case they contain nitrogen. (*ii*) The usual method of detecting nitrogen is by fusing the substance in an ignition tube with a small piece of metallic sodium; the mixture is at first heated gently and finally to the red heat. The hot end of the ignition tube is dipped into water in a dish, and broken. The contents are boiled and filtered, and a small quantity of ferrous sulphate added. The mixture is boiled and acidified with hydrochloric acid and $FeCl_3$ added. A blue precipitate or a bluish green colour would indicate the presence of nitrogen.

The nitrogenous compounds when heated with sodium form sodium cyanide, and the solution is alkaline. Ferrous sulphate with an alkali forms ferrous hydroxide which reacts with sodium cyanide to give sodium ferrocyanide. When acidified with hydro-

chloric acid, and on the subsequent oxidation in air, one gets ferric chloride also. Ferric ions with ferrocyanide give the Prussian blue colour:

$$Fe(OH)_2+6NaCN=Na_4Fe(CN)_6+2NaOH$$

$$3Na_4Fe(CN)_6+4FeCl_3=Fe_4[Fe(CN)_6]_3+12NaCl.$$

Detection of Halogens—Halogens are also tested in the above fusion of the compound with *sodium*. If the organic c m-pound contains halogens, sodium halide would be formed. The solution is acidified with nitric acid, and tested with silver nitrate, as in the inorganic analysis. If nitrogen is also present in the compound, the cyanide is formed on fusion which would interfere with the halide test. In such cases, hydrocyanic acid is expelled by boiling with strong nitric acid.

Another method for detection is to heat a copper wire in the Bunsen flame till it is black and ceases to give a blue flame. Now the hot end of the wire is dipped in the substance to be tested and again introduced in the flame. A green or blue coloration would indicate the presence of halogen.

Detection of Sulphur—Fuse the substance with sodium as above, and filter. Take a few drops of the solution on a watch glass, and add a drop of fresh sodium nitroprusside solution. A brilliant violet coloration would indicate the presence of sulphur.

If nitrogen and sulphur are both present, sodium thiocyante would be produced in the fusion reaction. Acidify the solution with hydrochloric acid and add ferric chloride. A blood-red coloration would indicate the simultaneous presence of sulphur and nitrogen.

Another method of detecting sulphur is to fuse the substance with sodium carbonate-potassium nitrate mixture (or with sodium peroxide). Sulphur is oxidised to sulphate; the solution is acidified with hydrochloric acid and tested with barium chloride.

If phosphorus is also present, the fusion with sodium peroxide forms phosphate which can be tesed with nitric acid and ammonium molybdate. The fusion is best done in a nickel crucible.

SECTION II

DETERMINATION OF BOILING AND MELTING POINTS

Melting Point Determination—This may be done in a beaker or Kjeldahl flask. A small beaker of 50 ml. capacity would be sufficient. In it take some strong sulphuric acid or glycerol. A very small quantity of the substance is taken in a capillary tube,

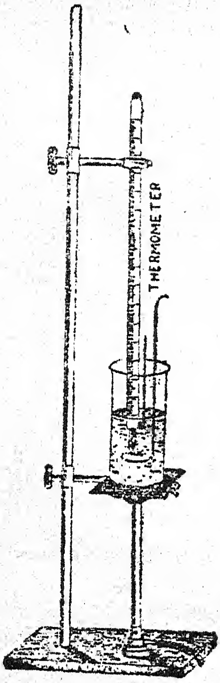

Fig. 11

closed at one end. The capillary is adhered to the thermometer by simply moistening it with concentrated sulphuric acid. The acid is gradually and cautiously heated; it is constantly stirred with a stirrer, and the temperature at which the substance melts is noted (fig. 11). This is the melting point.

Boiling point Determination—As the purity of a liquid is ascertained by determining its boiling point, it is necessary to find it out. A fractionating flask is taken and connected with a condenser. The neck of the flask is closed with a cork and a thermometer is introduced through it. The bulb of the thermometer is placed just a little below the side outlet tube. A few pieces of broken glass or porcelain are introduced into the liquid to prevent bumping. If the liquid boils above 125°, the condenser can be replaced by a long glass tube without a water jacket.

The liquid is placed in the flask, about one-third full. It is slowly heated and the temperature noted when it begins to distil. If the temperature is constant for a period of one-third distillation, the liquid may be regarded as pure.

If the quantity of the liquid is small, a test tube may be fitted with a cork provided with two holes, (Fig. 12)—one for the thermometer and the other for a tube bent at right angles. The latter tube may be connected with a short wide tube to act as condenser. The thermometer of the bulb is about an inch above the liquid.

Fractional Distillation—When the boiling points of two liquids are fairly apart, they may be separated by fractionation. An apparatus similar to one described above for the boiling point determination is set up. The liquid of a lower boiling point would distil over first, and as soon as it has almost distilled over, the boiling point will suddenly rise and become constant at a higher point. Another portion may be distilled over at this temperature.

Sometimes when the boiling points of two liquids are fairly close together, a fractionating column is employed. It consists of a series of pear-shaped bulbs. The Hempel's fractionation column is provided with glass beads. Some of them are provided with

glass discs. Some times the distillation flask itself is provided with fractionating bulbs in the neck.

The principle of fractionating columns may be thus realised: The vapour given off from the mixture consists of a larger proportion of the more volatile constituent than that in the liquid. While passing through the fractionation column, the liquid with higher boiling point is partially condensed, and runs back in the distillation flask, and the one with lower boiling point distils over. The distillate received consists of the more volatile portion only. The liquid in the flask becomes richer in the one with a higher boiling point. By this process, it is possible to affect a separation when the boiling points of the two liquids differ by a few degrees only, whereas without a fractionating column, a difference of at least 20-30° is necessary.

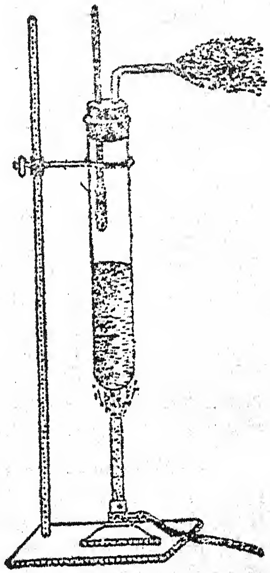

Fig. 12

Steam Distillation—This is one of the common methods of isolation and purification of organic substances, both solid and liquid. The substance and a little water are placed in a flask which is connected with a condenser and heated on a gauze or sand bath. The flask is also connected through a tube with steam generator (which may be a simple copper flask filled with water, and fitted with a delivery and a safety vertical long glass tube). The steam

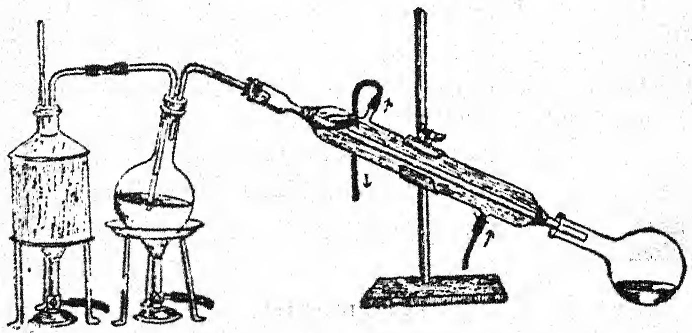

Fig. 13

from the generator bubbles through the mixture in the flask, and carries along with it the volatile constituent of the mixture(fig. 10). As it passes through the condenser, it gets cooled, and condenses along with it the volatile constituent. Very often the compound

volatilised with the steam is insoluble in water and separates as an oil or solid in the distillate.

Purification of Organic Substance—In the case of solid substances, the purification is effected by the processes of sublimation and crystallization. In the case of a liquid, the processes are washing and filtration, distillation—fractional and steam—and extraction with ether or some other solvent.

Crystallisation—The usual solvents used are water (b. p. 100°) ethyl alcohol (b. p. 78°), ether (b. p. 34·6°), petroleum ether (b. p. 60—90°), chloroform (b. p. 63°), and benzene (80·5°). A suitable solvent is selected out by trials, and then the solid dissolved in its minimum quantity; sometimes a higher temperature is preferable for the preparation of the solution. The solution is filtered and kept for crystallization. The crystals are removed by filtration; a filter pump may be used if necessary. The crystals are washed with the cold solvent, and then allowed to dry on a porous plate. Sometimes it is advisable to repeat the process depending on the relative solubilities of the components present in the mixture.

Sublimation—The process is of limited use. It can be carried out under the atmospheric pressure or under a reduced pressure. Benzoic acid may be tried as an experiment. Mix it with common salt, and place it on the clock glass covered with an inverted funnel. Plug the stem of the funnel with glass wool or cotton or even with a light beaker. The clock glass is gently heated on a sand bath. benzoic acid sublimes, and collects in the colder parts of the funnel. Camphor may also be similarly sublimed.

Extraction—An organic compound can often be separated from other substances, especially inorganic salts, by shaking with ether, separating the ethereal layer by the separating funnel, drying the solution with granular calcium chloride and removing ether by distillation (using a safety bath). The success in the process depends upon the partition coefficient of the substance between water and ether, *i.e.*, on the ratio:

$$\frac{\text{concentration in the ethereal solution}}{\text{concentration in the aqueous solution.}}$$

Benzene, chloroform and other liquids may also be used for extraction.

SECTION III

Qualitative Organic Analysis—A General Procedure.

The organic qualitative analysis consists of the identification of the following organic compounds given in aqueous or alcoholic solution :—

Oxalic acid, tartaric acid, succinic acid, citric acid, benzoic acid, salicylic acid, phenol or carbolic acid, acetic acid, formic acid, phthalic acid, pyrogallol, resorcinol, formaldehyde, acetaldehyde, chloroform, glucose, canesugar, chloral hydrate, acetone, methyl alcohol, ethyl alcohol, acetamide, benzamide, acetanilide, benzene, naphthalene, ether, glycerine, starch, urea, aniline, nitrobenzene, benzaldehyde, and iodoform.

The following important points should be remembered regarding these compounds :

(1) The acids may be given as such in which case the solution will be acidic or they may be given as sodium, potassium or ammonium salts, in which case the solution may be neutral.

(2) The following substances are not much soluble in water and *are*, therefore, *given in alcoholic solutions*. In such cases you will be asked to neglect alcohol :—

(i) *Solids given in alcoholic solution*—Benzoic acid, salicylic acid, phthalic acid, naphthalene, iodoform, benzamide and acetanilide.

(ii) *Liquids given in alcoholic solution*—Ether, benzene, phenol, chloroform, nitrobenzene, aniline and benzaldehyde.

But if benzoic, salicylic and phthalic acids are given in the form of sodium salts, they are given in water. Also if aniline is given as hydrochloride or sulphate, it is given in aqueous solution. This solution is strongly acidic and is, therefore, confused for some acid.

Preparation of neutral solution—If the solution supplied is acidic, it should be made neutral by *one* of the following proceses:—

(*a*) Take the solution in a beaker and put a piece of litmus paper into it. Now add sodium carbonate solution to it gradually, shaking all the time with a glass rod till it becomes slightly alkaline as indicated by the colour of the litmus paper turning blue. Then add a little dilute nitric acid so that the solution just becomes acidic (the litmus paper turns red). Add a small amount of ammonium hydroxide so that the solution becomes just alkaline (the litmus paper again turns blue). Now boil the solution till the excess of ammonia is completely driven off and there is no smell of ammonia in the solution. The solution is now neutral.

(*b*) Take the acidic solution in a beaker and add a few drops of phenolphthalein solution to it. Now add to it gradually drop by drop a dilute solution of caustic soda, shaking all the time, till the faint light pink colour just appears as in titrations.

Care should be taken that the alkali is not in excess otherwise there would be a lot of confusion in the analysis. In the first

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31. Find out the purity of hypo sample, $Na_2S_2O_3.5H_2O$, of which 30 g. were dissolved in a litre; 20 ml. of the solution when titrated with $N/20$ iodine solution required 15 ml. (*Ans.* 62·05 per cent).

32. How many grams of iodine be taken per litre, so that 10 ml. of the solution may require 15 ml. of $N/10$ As_2O_3 in titration? (*Ans.* 9·519 g.).

33. 10 ml. of a solution of $KMnO_4$, added to KI solution, liberated iodine, corresponding to 8·6 ml. of $N/20$ hypo solution. Find out the strength of $KMnO_4$ solution in grams per litre. (*Ans.* 1·359 g.).

34. How many grams of iodine will be liberated from KI solution by a copper sulphate solution which gives 0·4 gram of CuO on precipitation with alkali? (*Ans.* 0·638 g.).

35. 10 ml. of a solution of potassium dichromate liberated iodine from KI, which required 12 ml. of $N/20$ hypo solution for titration. Find out the strength of $K_2Cr_2O_7$ solution in grams per litre. (*Ans.* 2.9418 g.).

36. How many grams of ferric oxide, Fe_2O_3, would be obtained from 50 ml. of a solution of ferric chloride of which 10 ml. when titrated iodometrically require 8 ml. of $N/20$ hypo solution, the reaction is:

$$2FeCl_3+2KI=2FeCl_2+2KCl+I_2.$$

(*Ans.* 0.1597 g.).

37. 10 grams of a bleaching powder sample were dissolved to 250 ml. solution. 25 ml. of the solution were added to KI solution taken in excess and acidified with acetic acid. The iodine liberated was titrated with $N/2$ hypo solution. If the available chlorine is 30 per cent., find out in ml. the hypo solution required.

$$CaOCl_2 \equiv Cl_2 \equiv 2I.$$

(*Ans.* 17·03 ml.).

38. A sample of pyrolusite weighed 2 grams. The sample contains 60 per cent of pure MnO_2. It was heated with strong HCl, and the chlorine liberated was passed through a KI solution. The iodine solution was diluted to 200 ml. How many ml. of $N/20$ hypo would be required to react with 10 ml. of this diluted iodine solution.

$$MnO_2+4HCl=MnCl_2+Cl_2+2H_2O.$$

$$MnO_2 \equiv Cl_2 \equiv 2I.$$

(*Ans.* 22·7 ml.)

39. How would you prepare and standardise an $N/10$ solution of silver nitrate?

0·22 g. of a mixture of NaCl and KCl were titrated with 0·922 $N/10$ solution of $AgNO_3$, and required 33 ml. for complete reaction. What are the percentages of NaCl and KCl in the mixture?

(*Ans.* NaCl 39·6 per cent, KCl 60·4 per cent.).

40. 1·137 g. of pure iron were dissolved in an acid and raised to 250 ml.; 25 ml. of this ferrous solution when titrated with a $K_2Cr_2O_7$ solution, required 21.1 ml. of the dichromate solution. Find out the strength of the dichromate solution in grams per litre. (*Agra. Univ.*, *B.Sc.*, 1945). (*Ans.* 4·73 g.).

41. 0·261 g. of a sample of pyrolusite was heated with an excess of HCl and the chlorine evolved was passed into a solution of KI. The liberated iodine required 90 ml. of $N/30$ hypo. Calculate the percentage of pure MnO_2 present in the ore. (*Agra Univ.*, *B.Sc.*, 1942). (*Ans.* 50%).

42. How many grams of iodine will be liberated from a strong solution of KI when 100 ml. of copper sulphate solution containing 24·96 g. of the crystalline salt ($CuSO_4.5H_2O$) per litre are added to it? Give full equations of the reaction. (*Agra Univ.*, *B.Sc.*, 1944). *Ans.* 1·2692 g.).

43. Calculate in grams per litre the amount of ferrous and ferric iron present in a solution containing both from the following data:

25 ml. of the iron solution required for titration 24 ml. of the standard $KMnO_4$ solution. 100 ml. of the same solution were reduced completely with zinc and sulphuric acid, and the reduced solution was diluted to 250 ml.; 50 ml. of this dilute solution required 36·75 ml. of the same $KMnO_4$ solution.

The solution of $KMnO_4$ was titrated against $N/10$ oxalic acid and it was found that 25 ml. of $N/10$ oxalic acid were equivalent to 37·5 ml. of $KMnO_4$. (*B. H. U.*, *B. Sc.*, 1936). (*Ans.* Ferrous 3·57 g., ferric 3·266 g.).

44. How is a decinormal solution of "hypo" prepared?

100 ml. of a solution of NaCl and copper sulphate gave 1·434 g. of AgCl in a quantitative experiment. Another 100 ml. of the same solution on the addition of an excess of KI consumed 100 ml. of $N/10$ hypo. Find the amounts of NaCl and crystallised copper sulphate $CuSO_4$. $5H_2O$, in grams per litre. (*Alld. Univ.*, *B.Sc.*, 1957). (*Ans.* NaCl 5·845 g.; copper sulphate 24·97 g.).

45. One gram of pyrolusite is treated with an excess of concentrated HCl and the chlorine evolved is passed through KI solution in bulbs. This solution together with the liberated iodine, is diluted to 250 ml. and on titration with $N/50$ $Na_2S_2O_3$ solution, 25 ml. of the former are found equivalent to 31 ml. of the latter. Calculate the percentage of MnO_2 in the mineral. (*Alld. Univ., B. Sc.*, 1935). (*Ans.* 26·24 per cent).

46. 0.2 g. of a sample of pyrolusite, when warmed with excess of hydrochloric acid, and the evolved chlorine passed into excess of potassium iodide solution, required for the liberated iodine 30 ml. of $N/10$ thiosulphate solution. What is the percentage of pure manganese dioxide? (*Agra Univ., B.Sc.*, 1932. (*Ans.* 30·10 per cent).

47. Indicate the use of sodium thiosulphate in analytical chemistry.

0·2915 g. of a manganese ore was heated with hydrochloric acid and the chlorine evolved was passed into a solution of potassium iodide. The liberated iodine required 20.5 ml. of 0·1N sodium thiosulphate solution. Calculate the percentage of manganese dioxide in the ore. (*Agra Univ., B. Sc.*, 1935). (*Ans.* 13·3 per cent.)

48. Explain fully, with equations, the reactions underlying the analytical process in the titration of iron with permanganate and dichromate. (*Alld. Univ., B. Sc.*, 1945).

49. A quantity of $KMnO_4$ was boiled with hydrochloric acid and the gas evolved was led into a solution of KI. When the reaction was complete, the iodine liberated was titrated with a solution of sodium thiosulphate containing 124 g. of $Na_2S_2O_3.5H_2O$ per litre. It was found that exactly 60 ml. were required to decolourise the solutions of iodine. What weight of $KMnO_4$ was used? (*Agra Univ. B.Sc.*, 1947). (*Ans.* 0.9486 g.).

50. 0·6 of a sample of pyrolusite was boiled with 210 ml. of decinormal oxalic acid and excess of dilute sulphuric acid. The liquid was then filtered and the residue washed. The filtrate and washings were then mixed and made up to 500 ml. in a measuring flask. 100 ml. of this solution required 50 ml. of $N/30$ $KMnO_4$ solution. Calculate the percentage of MnO_2 in the given sample. (*Agra Univ., B. Sc.*, 1946; *Alld. Univ., B. Sc., II*, 1957). (*Ans.* 84·58%).

51. 1.137 g. of pure iron were dissolved in an acid and raised to 250 ml.; 25 ml. of this ferrous solution when titrated with $K_2Cr_2O_7$ solution required 21·1 ml. of the dichromate solution. Find out the strength of the dichromate solution in grams per litre. (*Agra Univ., B.Sc.*, 1945). (*Ans.* 9·46 g.).

52. Calculate the number of ml. of potassium dichromate solution containing 4·9 g. per litre of the salt required to oxidise 0·5 g. of iron dissolved in dilute sulphuric acid. In an actual experiment, 88·5 ml. were required. How do you account for the difference? (*Agra Univ., B. Sc.* 1948). (*Ans.* 89.3 ml.)

53. 0·2828 g. of iron wire was dissolved in excess of dilute sulphuric acid and the solution made up to 100 ml.; 20 ml. of this solution required 30 ml. of *N*/30 potassium dichromate solution for exact oxidation. Calculate the percentage purity of the wire. (*Agra Univ., B Sc.*, 1949). (*Ans.* 99%).

54. 0.5 g. of a sample of a bleaching powder was suspended in water and excess of KI added. On acidifying with dilute sulphuric acid, iodine was liberated which required 50 ml. of *N*/10 $Na_2S_2O_3 . 5H_2O$ solution. Calculate the percentage of available chlorine in the bleaching powder. Give equations. (*Agra Univ., B. Sc.*, 1950). (*Ans.* 35·50%).

55. How can a standard solution of copper sulphate be prepared? How would you proceed to determine the percentage purity of a given copper sulphate sample (*a*) gravimetrically, and (*b*) volumetrically. (*Alld. Univ., B. Sc. II*, 1957).

PART VII

Organic Substances and their Indentification

SECTION I

DETECTION OF ELEMENTS IN ORGANIC COMPOUNDS

Detection of Carbon and Hydrogen. All organic compounds contain carbon, and it is usually not necessary to detect carbon in them, unless one intends distinguishing them from inorganic. (i) Most organic substances char when strongly heated. They can be taken on a metallic spatula or on the blade of a knife and tested. (ii) Some of them blacken when heated with concentrated sulphuric acid. (iii) In case of those substances which do not answer these tests, they may be dried, powdered, and mixed with seven times their weight of powdered dry *copper oxide*, and strongly heated. This may be done in a dry test tube, fitted with cork and a delivery tube. The tube is clamped horizontally and heated. The gases evolved are allowed to bubble through lime water. If the latter is rendered turbid, the presence of carbon is established.

The formation of water drops on the cooler sides of the test tube indicates the presence of *hydrogen* in the compound. If the upper portions of the tube are dusted with anhydrous copper sulphate the presence of even traces of moisture can be detected by the blue colour, which copper sulphate assumes after absorbing moisture.

Detection of Nitrogen— (*i*) Some of the compounds, evolve ammonia, when strongly heated with soda-lime in a hard glass test tube, in case they contain nitrogen. (*ii*) The usual method of detecting nitrogen is by fusing the substance in an ignition tube with a small piece of metallic sodium; the mixture is at first heated gently and finally to the red heat. The hot end of the ignition tube is dipped into water in a dish, and broken. The contents are boiled and filtered, and a small quantity of ferrous sulphate added. The mixture is boiled and acidified with hydrochloric acid and $FeCl_3$ added. A blue precipitate or a bluish green colour would indicate the presence of nitrogen.

The nitrogenous compounds when heated with sodium form sodium cyanide, and the solution is alkaline. Ferrous sulphate with an alkali forms ferrous hydroxide which reacts with sodium cyanide to give sodium ferrocyanide. When acidified with hydro-

chloric acid, and on the subsequent oxidation in air, one gets ferric chloride also. Ferric ions with ferrocyanide give the Prussian blue colour:

$$Fe(OH)_2 + 6NaCN = Na_4Fe(CN)_6 + 2NaOH$$

$$3Na_4Fe(CN)_6 + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12NaCl.$$

Detection of Halogens—Halogens are also tested in the above fusion of the compound with *sodium*. If the organic c m-pound contains halogens, sodium halide would be formed. The solution is acidified with nitric acid, and tested with silver nitrate, as in the inorganic analysis. If nitrogen is also present in the compound, the cyanide is formed on fusion which would interfere with the halide test. In such cases, hydrocyanic acid is expelled by boiling with strong nitric acid.

Another method for detection is to heat a copper wire in the Bunsen flame till it is black and ceases to give a blue flame. Now the hot end of the wire is dipped in the substance to be tested and again introduced in the flame. A green or blue coloration would indicate the presence of halogen.

Detection of Sulphur—Fuse the substance with sodium as above, and filter. Take a few drops of the solution on a watch glass, and add a drop of fresh sodium nitroprusside solution. A brilliant violet coloration would indicate the presence of sulphur.

If nitrogen and sulphur are both present, sodium thiocyante would be produced in the fusion reaction. Acidify the solution with hydrochloric acid and add ferric chloride. A blood-red coloration would indicate the simultaneous presence of sulphur and nitrogen.

Another method of detecting sulphur is to fuse the substance with sodium carbonate-potassium nitrate mixture (or with sodium peroxide). Sulphur is oxidised to sulphate; the solution is acidified with hydrochloric acid and tested with barium chloride.

If phosphorus is also present, the fusion with sodium peroxide forms phosphate which can be tesed with nitric acid and ammonium molybdate. The fusion is best done in a nickel crucible.

SECTION II

DETERMINATION OF BOILING AND MELTING POINTS

Melting Point Determination—This may be done in a beaker or Kjeldahl flask. A small beaker of 50 ml. capacity would be sufficient. In it take some strong sulphuric acid or glycerol. A very small quantity of the substance is taken in a capillary tube,

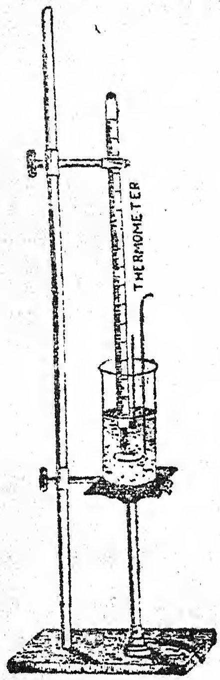

Fig. 11

closed at one end. The capillary is adhered to the thermometer by simply moistening it with concentrated sulphuric acid. The acid is gradually and cautiously heated; it is constantly stirred with a stirrer, and the temperature at which the substance melts is noted (fig. 11). This is the melting point.

Boiling point Determination—As the purity of a liquid is ascertained by determining its boiling point, it is necessary to find it out. A fractionating flask is taken and connected with a condenser. The neck of the flask is closed with a cork and a thermometer is introduced through it. The bulb of the thermometer is placed just a little below the side outlet tube. A few pieces of broken glass or porcelain are introduced into the liquid to prevent bumping. If the liquid boils above 125°, the condenser can be replaced by a long glass tube without a water jacket.

The liquid is placed in the flask, about one-third full. It is slowly heated and the temperature noted when it begins to distil. If the temperature is constant for a period of one-third distillation, the liquid may be regarded as pure.

If the quantity of the liquid is small, a test tube may be fitted with a cork provided with two holes, (Fig. 12)—one for the thermometer and the other for a tube bent at right angles. The latter tube may be connected with a short wide tube to act as condenser. The thermometer of the bulb is about an inch above the liquid.

Fractional Distillation—When the boiling points of two liquids are fairly apart, they may be separated by fractionation. An apparatus similar to one described above for the boiling point determination is set up. The liquid of a lower boiling point would distil over first, and as soon as it has almost distilled over, the boiling point will suddenly rise and become constant at a higher point. Another portion may be distilled over at this temperature.

Sometimes when the boiling points of two liquids are fairly close together, a fractionating column is employed. It consists of a series of pear-shaped bulbs. The Hempel's fractionation column is provided with glass beads. Some of them are provided with

glass discs. Some times the distillation flask itself is provided with fractionating bulbs in the neck.

The principle of fractionating columns may be thus realised: The vapour given off from the mixture consists of a larger proportion of the more volatile constituent than that in the liquid. While passing through the fractionation column, the liquid with higher boiling point is partially condensed, and runs back in the distillation flask, and the one with lower boiling point distils over. The distillate received consists of the more volatile portion only. The liquid in the flask becomes richer in the one with a higher boiling point. By this process, it is possible to affect a separation when the boiling points of the two liquids differ by a few degrees only, whereas without a fractionating column, a difference of at least 20-30° is necessary.

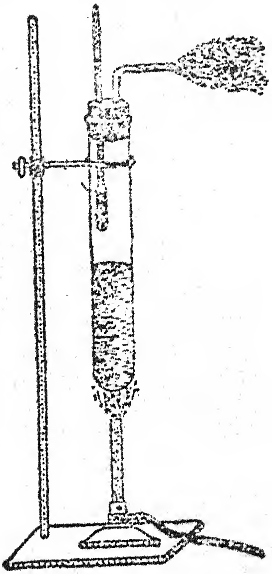

Fig. 12

Steam Distillation—This is one of the common methods of isolation and purification of organic substances, both solid and liquid. The substance and a little water are placed in a flask which is connected with a condenser and heated on a gauze or sand bath. The flask is also connected through a tube with steam generator (which may be a simple copper flask filled with water, and fitted with a delivery and a safety vertical long glass tube). The steam

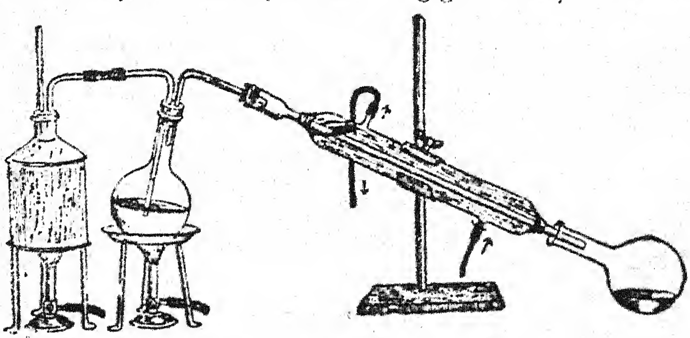

Fig. 13

from the generator bubbles through the mixture in the flask, and carries along with it the volatile constituent of the mixture(fig. 10). As it passes through the condenser, it gets cooled, and condenses along with it the volatile constituent. Very often the compound

volatilised with the steam is insoluble in water and separates as an oil or solid in the distillate.

Purification of Organic Substance—In the case of solid substances, the purification is effected by the processes of sublimation and crystallization. In the case of a liquid, the processes are washing and filtration, distillation—fractional and steam—and extraction with ether or some other solvent.

Crystallisation—The usual solvents used are water (b. p. 100°) ethyl alcohol (b. p. 78°), ether (b. p. 34·6°), petroleum ether (b. p. 60—90°), chloroform (b. p. 63°), and benzene (80·5°). A suitable solvent is selected out by trials, and then the solid dissolved in its minimum quantity; sometimes a higher temperature is preferable for the preparation of the solution. The solution is filtered and kept for crystallization. The crystals are removed by filtration; a filter pump may be used if necessary. The crystals are washed with the cold solvent, and then allowed to dry on a porous plate. Sometimes it is advisable to repeat the process depending on the relative solubilities of the components present in the mixture.

Sublimation—The process is of limited use. It can be carried out under the atmospheric pressure or under a reduced pressure. Benzoic acid may be tried as an experiment. Mix it with common salt, and place it on the clock glass covered with an inverted funnel. Plug the stem of the funnel with glass wool or cotton or even with a light beaker. The clock glass is gently heated on a sand bath. benzoic acid sublimes, and collects in the colder parts of the funnel. Camphor may also be similarly sublimed.

Extraction—An organic compound can often be separated from other substances, especially inorganic salts, by shaking with ether, separating the ethereal layer by the separating funnel, drying the solution with granular calcium chloride and removing ether by distillation (using a safety bath). The success in the process depends upon the partition coefficient of the substance between water and ether, *i.e.*, on the ratio:

$$\frac{\text{concentration in the ethereal solution}}{\text{concentration in the aqueous solution.}}$$

Benzene, chloroform and other liquids may also be used for extraction.

SECTION III

Qualitative Organic Analysis—A General Procedure.

The organic qualitative analysis consists of the identification of the following organic compounds given in aqueous or alcoholic solution :—

Oxalic acid, tartaric acid, succinic acid, citric acid, benzoic acid, salicylic acid, phenol or carbolic acid, acetic acid, formic acid, phthalic acid, pyrogallol, resorcinol, formaldehyde, acetaldehyde, chloroform, glucose, canesugar, chloral hydrate, acetone, methyl alcohol, ethyl alcohol, acetamide, benzamide, acetanilide, benzene, naphthalene, ether, glycerine, starch, urea, aniline, nitrobenzene, benzaldehyde, and iodoform.

The following important points should be remembered regarding these compounds :

(1) The acids may be given as such in which case the solution will be acidic or they may be given as sodium, potassium or ammonium salts, in which case the solution may be neutral.

(2) The following substances are not much soluble in water and *are*, therefore, *given in alcoholic solutions*. In such cases you will be asked to neglect alcohol :—

(i) *Solids given in alcoholic solution*—Benzoic acid, salicylic acid, phthalic acid, naphthalene, iodoform, benzamide and acetanilide.

(ii) *Liquids given in alcoholic solution*—Ether, benzene, phenol, chloroform, nitrobenzene, aniline and benzaldehyde.

But if benzoic, salicylic and phthalic acids are given in the form of sodium salts, they are given in water. Also if aniline is given as hydrochloride or sulphate, it is given in aqueous solution. This solution is strongly acidic and is, therefore, confused for some acid.

Preparation of neutral solution—If the solution supplied is acidic, it should be made neutral by *one* of the following processes:—

(*a*) Take the solution in a beaker and put a piece of litmus paper into it. Now add sodium carbonate solution to it gradually, shaking all the time with a glass rod till it becomes slightly alkaline as indicated by the colour of the litmus paper turning blue. Then add a little dilute nitric acid so that the solution just becomes acidic (the litmus paper turns red). Add a small amount of ammonium hydroxide so that the solution becomes just alkaline (the litmus paper again turns blue). Now boil the solution till the excess of ammonia is completely driven off and there is no smell of ammonia in the solution. The solution is now neutral.

(*b*) Take the acidic solution in a beaker and add a few drops of phenolphthalein solution to it. Now add to it gradually drop by drop a dilute solution of caustic soda, shaking all the time, till the faint light pink colour just appears as in titrations.

Care should be taken that the alkali is not in excess otherwise there would be a lot of confusion in the analysis. In the first

process, the possibility is avoided as the volatile alkali, *i.e.*, ammonia, if in excess, is driven off by boiling.

Residue—The residue of the supplied solution is prepared by evaporating a portion of the solution on a clock glass over a beaker. The beaker is filled three-fourths with water, the clock glass is placed over it and about 5 to 10 ml. of the solution is taken on it. The water in the beaker is boiled. When the solution is dried up, the clock glass is removed and the residue is examined.

In many cases the nature of the residue helps us a good deal to identify the substance. A solution on evaporation may leave a solid residue, a liquid residue or no residue. From this point of view, the substances may be classified as follows :—

(a) **Aqueous solution**

Solid residue			*Liquid residue*
Oxalic acid	Also their sodium salts.	Sodium formate	Glycerine
		Sodium acetate	
		Pyrogallol	
		Resorcinol	*No residue*
Succinic acid		Glucose	Acetic acid
		Cane sugar	Formic acid
		Chloral hydrate	Formaldehyde
Tartaric acid		Acetamide	Acetaldehyde
		Starch	Acetone
		Urea-	Methyl alcohol
Citric acid		Aniline Salt	Ethyl alcohol
Sodium benzoate			
Sodium salicylate			
Sodium phthalate			

(*b*) **Alcoholic sololution**

Solid residue	*Liquid residue*	*No residue*
Benzoic acid	Nitrobenzene	Chloroform
Phthalic acid	Aniline	Benzene
Salicylic acid	Carbolic acid	Ether
Benzamide	Benzaldehyde	
Acetanilide	(sometimes solid if	
Naphthalene	oxidised to benzoic	
Iodoform	acid during evaporation)	

Students are required to familiarise themselves with the characteristic residues. A few of the characteristics are given below:—

(*i*) White glistening plates—Salicylate, benzoic and salicylic acids.

(*ii*) Transparent sticky—Cane sugar, tartaric (weblike), citric (with stars at places), starch.

(*iii*) Reddish or brownish—Impure glucose, resorcinol, pyrogallol, aniline salts.

(*iv*) White, translucent, easily scratched with nails and gives soapy touch when macerated between fingers—Urea (and also sodium salts containing free alkali).

(*v*) Naphthalene, iodoform, acetamide, and chloral hydrate-may volatilise with steam, and not leave any solid residue.

(*vi*) Aniline, nitrobenzene, carbolic acid and benzaldehyde-may volatilise with steam and not leave any liquid residue.

(*vii*) Syrupy liquid, colourless—Glycerine.

(*viii*) Solid, white with blisters—Acetanilide.

(*ix*) Acetaldehyde and formaldehyde may polymerise to give slight residue.

The following substances are best identified with their residues:

Tartaric acid—resorcinol test.

Urea—biuret test.

Phthalic and succinic acids—fluorescein test.

Benzamide and acetanilide—caustic soda test.

Do not test in the aqueous solution for the substances which can only be given in alcohol and also do not test in the alcoholic solution for the substances which dissolve in water.

Smell—There are certain substances which can be identified by their characteristic smells. They are :—

Carbolic acid, formic acid, acetic acid, formaldehyde, acetaldehyde, benzaldehyde, chloroform, acetone, methyl alcohol, ethyl alcohol, benzene, naphthalene, ether, aniline, nitrobenzene and iodoform.

Of these benzene, naphthalene, ether and iodoform have got to be identified by their smell alone as there are no convenient tests for them.

Taste—Cane sugar, glycerine and glucose solutions have a sweet taste. Hence, an idea can be had by putting a drop on the tip of the tongue. Citric and tartaric acids may also be tested; Resorcinol is sweet with a bitter after-taste. Do not usually taste a substance.

How to proceed—Take about 5 ml. of the solution on a clock glass and heat it over a beaker filled with water. As the residue is thus being prepared, proceed with the analysis as given below and when the residue is ready it can be tested. This will save a lot of time. If the solution is acidic, it must be made neutral. The residue must be made out of the *original* solution and not of the prepared neutral solution.

CALCIUM CHLORIDE GROUP

This test is given by oxalate, tartrate, succinate, and citrate.

Take a portion of the *neutral* solution and add to it a solution of calcium chloride.

(*a*) An immediate precipitate—*Oxalate*.

(*b*) A precipitate on shaking vigorously and scratching sides of the test tube with glass rod—*Tartrate* (usually) or *succinate* (rarely gives the precipitate).

(*c*) A precipitate only on boiling and scratching—*Citrate*.

They can be confirmed as follows :—

Oxalic acid—(*i*) The precipitate obtained on adding $CaCl_2$ to the neutral solution is insoluble in acetic acid.

(*ii*) The above precipitate decolourises $KMnO_4$ solution in presence of mineral acids on warming.

Tartaric acid—(*i*) The precipitate obtained on adding $CaCl_2$ to the neutral solution is soluble in excess of acetic acid (distinction from oxalic acid).

(*ii*) The residue of the acidic solution is very characteristic (web like).

(*iii*) The neutral solution reduces the ammoniacal silver nitrate solution (2 ml. of $AgNO_3$, 1 drop of ammonia)—On heating, a silver mirror is obtained.

(*iv*) Treat the residue with twice the amount of resorcinol and a few drops of conc. H_2SO_4 and warm. A red colour is obtained (no red colour in the case of citric acid, hence distinction). If pyrogallol is used instead of resorcinol, the colour obtained is violet or blue instead of red.

Succinic acid—(*i*) Neutral solution + $FeCl_3$ solution in cold—a buff or brown precipitate.

(*ii*) Heat a portion of the residue in a dry test tube. Vapours having irritating smell (of burnt leather) are given out.

(*iii*) *Fluorescein test*—Heat carefully a portion of the dry residue with twice the amount of resorcinol and about 2 drops of conc. H_2SO_4 in a dry test tube (or on a porcelain piece) till it becomes orange-red. Pour the contents of the test tube into a beaker containing water to which caustic soda has been added. The solution shows yellow-green fluorescence.

(*iv*) Succinic acid is soluble in water. If the given solution is aqueous and acidic, it is succinic (distinction from phthalic).

Citric acid—(*i*) Heat the neutral solution with ammoniacal silver nitrate solution. There is no reduction of ammoniacal silver and no mirror is obtained (distinction from tartaric acid).

(*ii*) The residue is characteristic. It is transparent and sticky with formation of stars at places.

FERRIC CHLORIDE GROUP

This test is given by *phenol*, *resorcinol*, *pyrogallol*, *salicylate*, *formate*, *benzoate*, *and acetate* and also by *succinate*.

The ferric chloride solution supplied in the shelf should be diluted for this. To another portion of the neutral solution, add a *dilute* solution of neutral ferric chloride* *in cold*. (Do not heat).

(*a*) Red colour—formate or acetate.

(*b*) Violet or blue colour—carbolic acid, resorcinol or salicylic acid.

(*c*) Dark-pyrogallol.

(*d*) Buff or brown precipitate—benzoate or succinate.

They can be confirmed as follows: –

Formic acid—(*i*) A red colour is obtained on adding $FeCl_3$ to the neutral solution in cold.

(*ii*) The acid solution has a characteristic pungent smell.

(*iii*) Neutral solution + mercuric chloride—a white precipitate on warming, which turns black on further heating.

(*iv*) The neutral formate solutions reduce silver nitrate solution to black colour when warmed.

* Ferric chloride should be almost neutral. If it is highly acidic, neutralise it with a trace of ammonia solution.

Acetic acid—(*i*) The neutral solution gives red colour with ferric chloride in cold.

(*ii*) The acid solution has a characteristic smell of vinegar. If given as acetate, heat with dilute sulphuric acid—vinegar smell.

(*iii*) Solution+ammoniacal $AgNO_3$—It does not reduce this solution (distinction from formic acid).

Carbolic acid or Phenol—(*i*) The acid solution has a characteristic carbolic smell so very familiar. It is sparingly soluble in water and is usually given in alcohol or in very dilute aqueous solutions.

(*ii*) The solution of phenol gives a violet colour with ferric chloride which is destroyed on addition of acetic acid.

(*iii*) Solution+NH_4OH+bromine water, warm—a light blue colour is obtained which changes to light red on adding dilute hydrochloric or nitric acid.

Salicylic acid—(*i*) A violet colour with ferric chloride which persists on addition of acetic acid.

(*ii*) To the neutral solution, add a few drops of conc. H_2SO_4, shake and cool—white flakes of the free acid.

(*iii*) Add bromine water to the solution—a precipitate is obtained.

(*iv*) Heat a portion of the solid residue with conc. nitric acid. A yellow colour is obtained which is intensified on the addition of alkali.

(*v*) Heat another portion of the solid residue with methyl alcohol and conc. H_2SO_4. A sweet smell of the oil of winter green is obtained.

Pyrogallol—The fresh solution is colourless, but darkens on exposure to air.

(*i*) The solution reduces Fehling's solution.

(*ii*) The solution reduces silver nitrate solution.

(*iii*) Add excess of lime water or caustic soda to a portion of the solution and shake well; the solution turns red and then brown.

(*iv*) To the solution, add ferrous sulphate solution—blue or violet colour.

Resorcinol—(*i*) Heat the solution with caustic soda—a very characteristic greenish-yellow colour is obtained (a sure test).

(*ii*) Heat the residue with succinic or phthalic acid and 2 drops of conc. H_2SO_4 in a dry test tube or on a porcelain piece.

ORGANIC ANALYSIS

Substance	State	Soluble in	Residue	Smell	with $CaCl_2$ (in neutral sol.)	with $FeCl_2$ (in neutral sol.)	Fehling's sol.	Am. $AgNO_3$	with NaOH (in neutral sol.)	Special
Oxalic acid	solid	water	white	no	white ppt. insol. in acetic acid		—	—	—	—
Tartaric acid	,,	,,	transparent sticky	,,	crys. ppt. on shaking		—	mirror	—	Red col. with resorcin and conc. H_2SO_4.
Citric acid	,,	,,	,,	,,	ppt. on heating		—			
Succinic acid	,,	,,	white	,,	ppt. on shaking (difficult)	gel. reddish ppt.	—	—	—	Fluorescein test with resorcin and conc. H_2SO_4.
Benzoic acid	,,	alcohol (salt sol. in H_2O)	white glistening	,,	no	buff ppt.	—	—	soluble	Aqueous sol. with conc. H_2SO_4—white ppt. on cooling.
Salicylic acid	,,	,,	,,	,,	,,	violet col. not discharged with acetic acid	—	—	,,	,, ,, ,,
Phenol	solid (m. p. 43°)	water, and also alcohol	slightly coloured (steam volatile)	carbolic	,,	violet col. discharged with acetic acid	—	—	—	Blue col. with ammonia+Br water: turns pink on adding HCl.
Resorcin	,,	water	brownish	no	,,	,,	reduces	reduces	yell. green	Fluorescein with phthalic acid+conc. H_2SO_4.
Pyrogallol	,,	,,	dark coloured	,,	,,	dark col.	light reduction	,,	brown	With $FeSO_4$ sol., violet col.
Acetic acid	liquid if free	,,	no (salt leaves)	vinegar if free	,,	red col.	no	no	no	Acetates give smell of vinegar with conc. H_2SO_4.
Formic acid	,,	,,	,,	SO_2 like if free	,,	,,	,,	reduces	,,	Neutral sol. reduces $HgCl_2$ to white ppt.; formates give SO_2 like smell with conc. H_2SO_4.
Phthalic acid	solid	alcohol	solid	no	,,	buff ppt.	,,	no	soluble	Fluorescence with resorcin+conc. H_2SO_4.
Formaldehyde	liquid	water	light white	pungent	,,	no	reduces to Cu	reduces	no	Pink col. in cold with Schiff's reagent.
Acetaldehyde	,,	,,	no	,,	,,	,,	reduces	,,	buggy smell yell. colour	,, ,,
Glucose	solid	,,	light brown sticky transparent	no	,,	,,	,,	mirror	yell. colour sweet smell	
Cane Sugar	,,	,,		,,	,,	,,	,,	—	—	On inversion with HCl (dil.) (add now NaOH), gives test of glucose.
Chloralhydrate	,,	,,	,,	disagreeable	,,	,,	(on inversion) reduces	mirror	smell of chloroform	With NaOH+resorcin, pink colour.
Acetamide	,,	,,	light	light mousy	,,	,,	no	no	smell of NH_3	
Urea	,,	,,	white soapy	no	,,	,,	,,	,,	no	On heating, the residue melts; ammonia given off, gives violet col. with $CuSO_4$+NaOH (biuret test).
Starch	,,	,,	sticky transparent	,,	,,	,,	reduces on hydrolysis	,,	,,	With iodine sol., blue colour.
Acetone	liquid	,,	no	sweet	,,	,,	no	,,	,,	(a) With NaOH (or NH_4OH)+iodine, iodoform smell. (b) With ammonia and Na nitroprusside, violet colour.
Methyl alcohol	,,	,,	,,	,,	,,	,,	,,	,,	,,	With salicylic acid—conc. H_2SO_4—oil of winter green smell.
Ethyl alcohol	,,	,,	,,	,,	,,	,,	,,	,,	,,	With NaOH+iodine—iodoform smell.
Glycerine	,,	,,	liquid syrup sweet	no	,,	,,	,,	,,	,,	Dunstan's test, borax-phenolphthalein col. destroys in cold but reappears on heating.
Benzene	(0·88 sp. gr.)	alcohol	no	petroleum	,,	,,	,,	,,	,,	Burns with smoky flame.
Ether	(0·736 sp. gr.)	,,	,,	ethereal	,,	,,	,,	,,	,,	Cooling touch.
Toluene	liquid	,,	,,	chara[illegible]	,,	,,	,,	,,	,,	With $KMnO_4$, gives benzoic acid.
Chloroform	,,	,,	,,	sweet	,,	,,	reduces	,,	,,	With NaOH+resorcin, warm,→pink colour.
Aniline	,,	,,	steam volatile	chara[illegible]	,,	,,	no	,,	,,	Fumes with HCl conc.; with alpha-naphthol, $NaNO_2$ and dil. HCl→red col. On heating with Fe+HCl, gives aniline.
Nitrobenzene	,,	,,	,,	of bitter almonds	,,	,,	,,	,,	,,	
Benzamide	solid	,,	white	no	,,	,,	,,	,,	residue gives smell of NH_3	
Acetanilide	,,	,,	(blisters)	,,	,,	,,	,,	,,	residue gives smell of aniline	
Naphthalene	,,	,,	steam volatile	chara[illegible]	,,	,,	,,	,,	no	Picrate
Anthracene	,, (fluor).	hot benzene	bluish solid	no	,,	,,	,,	,,	,,	Picrate
Tribromaniline	solid	alcohol	white	,,	,,	,,	,,	,,	,,	Test for bromine.
	,,	,,		chara[illegible]	,,	,,	,,	,,	,,	Test for iodine.

Pour the contents into a beaker containing water and caustic soda solution: a green fluorescent colour is obtained.

(*iii*) It slightly reduces ammoniacal $AgNO_3$ solution.

(*iv*) It slightly reduces Fehling's solution.

(*v*) With ferric chloride, it gives violet blue colour which is discharged on adding acetic acid.

Benzoic acid—(*i*) A buff precipitate or the reddish brown colour is obtained on adding $FeCl_3$ to the neutral solution.

(*ii*) To the neutral solution, add a few drops of conc. H_2SO_4, shake, and cool—white flakes of the free acid (cf. salicylic acid).

(*iii*) The neutral solution gives no precipitate with $CaCl_2$ (distinction from succinate).

(*iv*) The residue does not give fluorescein test (distinction from succinic acid).

(*v*) If the acid is given as such in solution, it must be alcoholic as it is insoluble in water.

FLUORESCEIN TEST

This test is given by succinic acid and phthalic acid.

Heat a portion of the residue with resorcinol and one drop conc. H_2SO_4 in a dry test tube and pour the contents of the tube into a beaker containing water to which some caustic soda has been added. The formation of a yellow-green fluorescent colour shows the presence of succinic or phthalic acid.

The test is complimentary for resorcinol (see above).

Tests for succinic acid have already been given and phthalic acid may be confirmed as follows:—

Phthalic acid—(*i*) The neutral solution gives no precipitate with $CaCl_2$ (distinction from succinate).

(*ii*) The free acid is insoluble in water. It is given in alcohol, or dissolved in alkali (distinction from succinic).

(*iii*) Heat a portion of the solid residue in a dry test tube; vapours having choking smell are given out (distinguish from irritating vapours of succinic acid).

(*iv*) It furnishes the fluorescein dye, when its dry residue is heated with resorcinol and a drop of concentrated sulphuric acid. Fluorescence is observed on adding NaOH solution.

FEHLING'S SOLUTION GROUP

Add Fehling's solution* (obtained by adding Fehling's solution No. 2 to Fehling's solution No. 1, till the blue precipitate first formed disappears and an intense blue colour is obtained) to about 3 ml. of hot solution under examination; heat again. The formation of green, yellow, orange or red coloured precipitate *shows the presence of formaldehyde, acetaldehyde, chloral hydrate, chloroform, resorcinol, glucose or pyrogallol.* The inverted cane sugar and hydrolysed starch also give this test.

The tests for pyrogallol have already been given. Others may be confirmed as follows :—

Formaldehyde-(*i*) A pink colour is obtained on adding Schiff's reagent § to the solution *in cold.*

(*ii*) The solution has a characteristic odour. The nature of the smell is not changed on warming it with caustic soda solution.

(*iii*) The solution reduces ammoniacal silver nitrate solution.

Acetaldehyde—(*i*) A pink colour is obtained *in cold* on adding Schiff's reagent to the solution and shaking (do not heat).

(*ii*) The smell is offensive. On heating the solution with caustic soda, buggy odour is obtained and the colour becomes yellow (distinction from formaldhyde).

(*iii*) The solution reduces ammoniacal silver nitrate.

Chloral hydrate—(*i*) Heat a portion of the solution with caustic soda; an emulsion is formed and smell of chloroform is given. The sweet smell is not present in the original solution. The substance is given in water (distinction from chloroform).

(*ii*) A pink colour is obtained on adding resorcinol and caustic soda, and heating the solution.

(*iii*) The solution reduces ammoniacal silver nitrate.

Chloroform—(*i*) The solution gives an emulsion with water. (It is given as an alcoholic solution).

(*ii*) It has sweet and pleasant odour.

(*iii*) A pink colour is obtained on adding resorcinol and caustic soda to the solution and warming.

* Fehling's solution is obtained by adding sodium potassium tartrate or Rochelle salt and caustic soda to copper sulphate solution.

Fehling's solution No. I. It contains acidified copper sulphate solution.

Fehling's solution No. II. It contains sodium potassium tartrate and caustic soda.

§Schiff's reagent is magenta or fuchsine dye, decolourised by passing sulphur dioxide.

(*iv*) Heat a portion of the solution with aniline and caustic soda—a characteristic odour of phenyl isocyanate.

Glucose—(*i*) Heat the solution with caustic soda—a yellow colour.

(*ii*) The solution reduces ammoniacal silver nitrate to a mirror when warmed.

(*iii*) Add conc. H_2SO_4 to the solid residue. A yellow colour is obtained which changes to brown but no charring takes place (distinction from cane sugar).

CANE SUGAR AND STARCH

Take about 5 ml. of the solution in a test tube, add to it 1 ml. of dil. H_2SO_4 and boil. Now neutralise the acid with caustic soda in excess. A yellowish solution is obtained. Add to 3 ml. of this, a few drops of Fehling's solution,—the formation of a yellowis green to red precipitate (reduction) shows the presence of cane sugar or starch. (In the case of starch the hydrolysis takes place slowly. The starch solution should be boiled for *ten* minutes with about 5 ml. of *strong* hydrochloric acid, the acid is then neutralised with alkali and then tested with the Fehling's solution). They can be confirmed as follows:—

Cane sugar—(*i*) The solution is sweet and has a characteristic odour.

(*ii*) Add conc. H_2SO_4 to the solid residue—it is charred (distinction from glucose).

Starch—(*i*) To a dilute solution of iodine, add a few drops of the solution in *cold*, a blue colour is obtained.

(*ii*) The solution is not sweet (distinction from cane sugar).

CAUSTIC SODA GROUP

Heat a portion of the solution or solid residue (if the solution is alcoholic) with a strong caustic soda solution and note the smell and change in colour.

(*i*) *If the solution is aqueous*:—

(*a*) Smell of ammonia—ammonium salts of acids and acetamide.

(*b*) Smell of aniline—aniline salts.

(*c*) Smell of chloroform—chloral hydrate.

(*d*) Yellowish-green colour—resorcinol.

(e) Yellow colour—glucose.

(f) Yellow colour—with buggy smell—acetaldehyde.

(g) Brown colour—pyrogallol.

(ii) *If the solution is alcoholic*—Use the residue for tests.

(a) Smell of ammonia—benzamide.

(b) Oily drops and smell of aniline—acetanilide.

The tests for ammonium salts of acids, resorcinol, glucose, acetaldehyde and chloral hydrate have already been given. Others are confirmed as follows :—

Acetamide—(i) Smell of ammonia on heating the solution with caustic soda in excess. Heat for 5 minutes and add an excess of sulphuric acid—smell of acetic acid is obtained.

(ii) No precipitate or colour is obtained on adding $FeCl_3$ to a portion of the solution (distinction from ammonium acetate).

Benzamide—(i) On heating a portion of the solid residue with caustic soda, smell of ammonia is obtained. When this solution is cooled and acidified with conc. sulphuric acid, benzoic acid is obtained as a precipitate and can be tested as shown in the case of benzoic acid.

(ii) The solution does not give any colour or precipitate with $FeCl_3$ (distinction from ammonium benzoate).

(iii) The residue is characteristic.

Acetanilide—(i) On heating a portion of the solid residue with strong caustic soda solution, oily globules are obtained and aniline given out, which can be identified by its smell or by α naphthol test as given in the case of aniline. On acidifying this solution with dilute H_2SO_4, smell of acetic acid is obtained (generally the smell of acetic acid is masked by that of aniline).

(ii) The residue is very characteristic when the solution is evaporated and alcohol is completely driven out; the residue is obtained in the form of blisters which rise up and then burst out.

IODOFORM TEST

Heat a portion of the solution with caustic soda and iodine. The solution becomes yellow and precipitate of iodoform having a characteristic smell is obtained in the case of *ethyl alcohol* and *acetone*.

They can be tested as follows :—

Ethyl alcohol—(*i*) It gives iodoform on heating with caustic soda and iodine.

(*ii*) Heat a portion of the solution with potassium permanganate in presence of dil. H_2SO_4—smell of acetaldehyde is obtained.

(*iii*) It does not give iodoform on heating with ammonium hydroxide and iodine (distinction from acetone).

Acetone—(*i*) It gives iodoform on heating with caustic soda and iodine and also with ammonium hydroxide and iodine.

(*ii*) The solution on treatment with a *freshly prepared* solution of sodium nitroprusside and ammonium hydroxide gives a violet colour.

SPECIFIC GROUP

The remaining substances do not come under any group. They have got their own individual tests with which they can be identified.

Methyl alcohol—(*i*) The solution has a characteristic smell.

(*ii*) On heating the solution with sodium salicylate and conc. sulphuric acid, smell of oil of winter green (methyl salicylate) is obtained.

(*iii*) On heating a portion of the solution with potassium permanganate in presence of dil. H_2SO_4, smell of formaldehyde is obtained.

Urea—The residue is characteristic with a soapy touch.

(*i*) On heating the residue in a dry test tube (or on a porcelain piece), it melts and smell of ammonia is given. Stop heating at this stage (do not heat too much) and add about two or three drops of caustic soda solution, and then one drop of dilute copper sulphate solution; a violet colour is obtained. This is called *biuret* test.

(*ii*) Heat a portion of the residue with conc. HNO_3 and cool : crystals of urea nitrate separate out.

Glycerine—Add one or two drops of phenolphthalein to a dilute solution of borax; a pink colour is obtained. Dilute it and then add the given solution to a portion of it, the pink colour is discharged. On heating, the colour *reappears*. This is called *Dunstan's test*.

The pink colour of borax solution in presence of phenolphthalein is also discharged by glucose and by free acids. But glucose reduces Fehling's solution whereas glycerine does not. Also in

the case of free acids, the discharged colour does not appear on heating, as it happens with glycerine.

Aniline—(*i*) It is tested by α-naphthol test. Add dilute hydrochloric acid to a portion of the solution and then sodium nitrite, gradually cooling all the time. Now take in a test tube an alkaline solution of α-naphthol and to it add the above solution gradually; a red colour is obtained. It is important that the first solution should be added to the alkaline solution of α-naphthol and not the latter to the former. (If the reverse process is followed, the result may not be satisfactory).

(*ii*) Add about 1 ml. of conc. H_2SO_4 to the solution; and to this now add some solid potassium dichromate; a blue colour is obtained.

(*iii*) Aniline vapours give white fumes when mixed with conc. HCl vapour (cf. ammonia).

Aniline can also be given in the form of salts, *e. g.*, hydrochloride or sulphate. In that case the solution will be strongly acidic but will not give test for any organic acid. It will give α-naphthol test for aniline quite all right.

Aniline salts, when heated with caustic soda solution, liberate oily drops of aniline with the characteristic smell.

Nitrobenzene—(*i*) It has a characteristic smell.

(*ii*) Heat a portion of the solution with zinc and dilute sulphuric acid. Nitrobenzene is reduced to aniline which can be tested with α-naphthol test.

Iodoform—It is given in alcoholic solution and possesses its very characteristic smell.

Ether, $C_2H_5OC_2H_5$—It also possesses a characteristic smell and causes cooling when it falls on any part of the body.

Ether is a mobile, neutral, pleasant smelling liquid, sp. gr. 0·736 at 0°; b. p. 35°, very volatile and highly inflammable.

Benzene—(*i*) It possesses a characteristic colour.

(*ii*) Take a few ml. in a dish and apply flame. It burns with a smoky flame.

Naphthalene—It is given in alcoholic solution and possesses a characteristic smell.

Benzaldehyde—(*i*) It reduces ammoniacal silver nitrate on warming, giving a bright mirror.

(*ii*) It does not reduce Fehling's solution.

(*iii*) Gives a white crystalline compound with $NaHSO_3$.

(*iv*) Hydrolyses to benzoic acid and benzyl alcohol with strong solution of NaOH.

SECTION IV

SYSTEMATIC IDENTIFICATION OF SIMPLE ORGANIC SUBSTANCES

In order to be successfully able to identify a given organic compound, it is necessary to proceed in a systematic manner. Attempts to identify it only by smell, colour, taste or even boiling and melting point determination is bound to lead one to a wrong conclusion. It is necessary, therefore, to make a start with preliminary analysis, *i. e.*, finding out the elements present. This will be followed by finding out the nature of groups corresponding to those elements. If a compound contains nitrogen, see if it is in the form of nitro group, cyanide group and so on. If it contains oxygen, see if it is present as hydroxy group, aldehydic group, ketonic group or carboxylic group. Having ascertained the various groups present, the melting or boiling point should be determined and efforts should be made to locate the compound in that particular group in the tables given below. One or two confirmatory tests, specially some colour reactions where possible, should now be performed. The final confirmation is to be made by preparing a derivative where possible. Details of specific tests like Dunstan's test or biuret test can be found in the book in sections dealing with organic identification.

1. Test for elements.

Lassaignes' Test—A little of the substance is heated to redness in a hard glass fusion tube with metallic sodium. The hot end of the tube is dipped into water contained in a small porcelain dish. The tube breaks and its contents get mixed with water. The solution is boiled and filtered. A little of the freshly prepared ferrous sulphate solution is added to it and it is boiled again. Now it is acidified with concentrated hydrochloric acid and cooled and one or two drops of ferric chloride solution are added. A blue colour or precipitate confirms the presence of nitrogen in the compound.

When an organic compund containing nitrogen is fused with sodium, sodium cyanide is formed and will be present in the solution along with caustic soda formed by the action of excess sodium on water.

$$Na+C+N \rightarrow NaCN \text{ (sodium cyanide)}$$

Sodium cyanide reacts with ferrous sulphate forming sodium ferrocyanide.

$$2NaCN + FeSO_4 = \underset{\text{ferrous cyanide.}}{Fe(CN)_2} + Na_2SO_4$$

$$Fe(CN)_2 + 4NaCN = Na_4Fe(CN)_6$$

Hydrochloric acid is used to dissolve the ferrous hydroxide formed by the action of caustic soda on ferrous sulphate.

Now ferric chloride reacts with sodium ferrocyanide to give Prussian blue, *i.e.*, ferric ferrocyanide.

$$4FeCl_3 + 3Na_4Fe(CN)_6 = \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

In some substances like diazo compounds or methyl acetanilide, the test fails. In such cases a mixture of potassium carbonate and magnesium powder sould be used in place of sodium.

Detection of sulphur—The presence of sulphur in an organic compound is also ascertained by the above Lassaignes' test.

If the organic compound under examination contains sulphur, this will be converted to sodium sulphide on fusion with sodium.

$$2Na + S = Na_2S$$

This can be tested as follows :—

(*i*) It gives a transient violet colour with a few drops of freshly prepared sodium nitroprusside solution

(*ii*) It produces a black stain on silver coin.

Nitrogen and sulphur present together—When both nitrogen and sulphur are present together in an organic compound, sodium thiocyanate or sodium sulphocyanide will be produced on fusion with sodium.

$$Na + C + N + S = NaCNS.$$

When this solution is acidified with hydrochloric acid and ferric chloride added, a blood red colour of ferric thiocyanate is produced.

$$3NaCNS + FeCl_3 = Fe(CNS)_3 = 3NaCl$$

Detection of halogens—When an organic substance containing a halogen is heated with sodium (see Lassaignes' test above for sulphur), the halogen is converted into sodium halide : $Na + Cl = NaCl$, $Na + Br, = NaBr$, $Na + I = NaI$. The filtrate is boiled with about 1 ml. of concentrated nitric acid to decompose cyanide,

and silver nitrate solution added to it. The formation of a curdy white precipitate soluble in ammonium hydroxide shows chloride.

$$NaCl + AgNO_3 = \underset{\text{white}}{AgCl} \downarrow + NaNO_3$$

A yellow precipitate indicates bromide or iodide.

$$NaBr + AgNO_3 = \underset{\text{yellow}}{AgBr} \downarrow + NaNO_3$$

$$NaI + AgNO_3 = \underset{\text{yellow.}}{AgI} \downarrow + NaNO_3$$

Distinction between bromide and iodide—To the solution containing bromine or iodine as sodium bromide or iodide, a little chloroform or carbon tetrachloride is added and then a few ml. of strong chlorine water. The tube is shaken well. If the chloroform or carbon tetrachloride layer turns brown, bromine is present and if it turns violet, iodine is present.

$2NaBr + Cl_2 = 2NaCl + Br_2$ (soluble in chloroform with brown colour).

$2NaI + Cl_2 = 2NaCl + I_2$ (soluble in chloroform with violet colour).

2. Test whether the compound is aliphatic or aromatic.

Burn a litle of the substance on a spatula. If it burns with a sooty flame, it is generally aromatic. If it burns with a nonsooty flame, it is aliphatic.

Confirmation may be made by boiling a little of the substance with conc. nitric acid. If the solution turns yellow, it is aromatic, otherwise it is aliphatic.

3. Test for unsaturation.

Find out whether the compound under examination is saturated or unsaturated. This can be done with the help of bromine water or potassium permanganate solution. In the case of unsaturated compounds, the colour is discharged in cold. (But if all the substances prescribed in the course are saturated, this test is not necessary).

4. Group test.

Now it is necessary to find out what groups are present in the compound. Some of the simple tests for various groups are given below :

(*a*) *Carboxylic group* (—COOH)—Sometimes a compound containing—COOH group may change the colour of blue litmus to red.

If the compound is soluble in water, make a solution of it in water and treat the solution with sodium bicarbonate. Effervescence *in cold* indicates presence of—COOH group.

If the compound is insoluble in water, treat a saturated solution of sodium bicarbonate with the substance in cold. Slow effervescence indicates the presence of a—COOH group.

(*b*) *Aldehydic group*—(—CHO)—See the reaction of the substance on Schiff's reagent *in cold*. If the colour is restored, presence of aldehydic group is indicated.

Heat a little of the substance with Fehling's solution—Reduction indicates the presence of an aldehydic group.

(*c*) *Ketonic group*—($>C=O$)—Treat the ketone with an aqueous solution of sodium bisulphite—Formation of a crystalline compound indicates the presence of an aldehydic or ketonic group.

Treat a small quantity of the substance with a few drops of sodium nitroprusside, followed by a drop of NaOH,—red colour indicates a ketone containing CH_3CO—group.

Add about 0·1 g. of powdered m-dinitrobenzene and then excess of NaOH solution to a small amount of the substance and shake; violet colour which gradually fades indicates ketones (benzophenone does not give this test).

(*d*) *Phenolic group*—Add to a dilute solution of the substance a few drops of dilute neutral ferric chloride—Formation of a blue, violet or green colour indicates the presence of phenolic hydroxy group. In this case, it should be noted that with hydroquinone, greenish black ppt. is obtained; a white ppt. changing its colour to violet indicates α-naphthol and green colour changing to white shows β-naphthol.

(*e*) *Alcoholic group*—Add a piece of dry sodium to a few drops of the liquid—Evolution of hydrogen indicates the presence of an alcoholic group (this will be given by phenols also).

If a compound contains larger number of alcoholic groups, it gives intense yellow colour with ferric chloride.

(*f*) *Esters*—To a little of the substance in water, add a drop of phenolphthalein and then a dilute solution of NaOH drop by drop, till a pink colour appears. Now heat it—the pink colour disappears showing the presence of ester group.

(*g*) *Carbohydrates*—Monosaccharides reduce Fehling's solution; polysaccharides do so after hydrolysis (see test of cane sugar, in the book p. 243).

(*h*) *Hydrocarbons*—If none of the above tests are obtained, the compound is a hydrocarbon.

(*i*) *Amino-group*—Dissolve the substance containing nitrogen in hydrochloric acid, cool it and gradually add sodium nitrite to it, cooling all the time. Add this to a cooled alkaline solution of α or β-naphthol, an orange-red dye indicates the presence of primary amino-group. In case of a secondary amino-group, a yellow oil is obtained on treatment with HNO_2.

(*j*) *Nitro-group*—Reduce the substance with Sn+HCl and then test for amino-group as above.

(*k*) *Amides*—Heat with alkali. Smell of ammonia is obtained.

5. Determination of melting and boiling points.

Next the melting points of solids and the boiling points of liquids should be determined and efforts should now be made to locate the substance in the charts given below according to the groups present.

6. Preparation of derivatives.

It is advisable to prepare the following derivatives in various cases :—

(*a*) *Hydrocarbons—Picrate*—Mix the saturated solution of the hydrocarbon in alcohol with a saturated solution of picric acid in alcohol; cool; a precipitate of picrate separates out.

Nitro-derivative—Treat a mixture of nitric acid and sulphuric acid with the substance; nitro-derivative is formed and can be crystallised.

(*b*) *Alcohol-Acetyl-derivative*—Treat a little of the substance with acetic anhydride and fused sodium acetate and reflux for one hour. Pour it in water. Filter and dry the precipitate formed.

(*c*) *Phenols and amino compounds*—Prepare acetyl derivative as above.

(*d*) *Aldehydes and ketones—Phenylhydrazone*—Treat a little of the substance in glacial acetic acid with phenylhydrazine and heat on water bath. Phenylhydrazone can be purified by crystallisation.

(*e*) *Carbohydrates—Osazone*—Prepare osazone as above using excess of phenylhydrazine.

(*f*) *Acids—Amide*—Prepare ammonium salt and distill it on a dish over sand bath. Collect the cooled vapour over an inverted funnel and separate the amide formed.

(*g*) *Ester*—Separate the acid by hydrolysis.

In individual cases derivatives are mentioned along with the compounds. The easiest one should be prepared.

A. Compounds containing C, H & O

HYDROCARBONS

Liquids

B. P.

80° *Benzene*, C_6H_6—M. P. 5°, sp. gr. 0·847 (20°), a colourless liq. immiscible with water, burns with smoky flame; on nitration yields nitrobenzene, B. P. 209°; and m-dinitrobenzene, M. P. 90°; on bromination yields bromobenzene, B. P. 175°; and p-dibromobenzene, M. P. 89°; picrate, M. P. 84°.

110° *Toluene*, $C_6H_5CH_3$—sp. gr. 0·871 (13°), colourless liquid with characteristic smell; on oxidation with alkaline $KMnO_4$ yields benzoic acid, M. P. 121°; 2 : 4 dinitroderivative, M. P. 70°; 2: 4: 6 trinitro-derivative. M. P. 82°.

Solids

M. P.

80° *Naphthalene*, $C_{10}H_8$—characteristic odour, burns with a smoky flame. Picrate, M. P. 149°; oxidised to phthalic acid, M. P. 195°.

ALCOHOLS

Liquids

B. P.

65° *Methyl alcohol* CH_3OH—sp. gr. 0·796 (20°), colourless; miscible with water; oxidn. by hot copper wire gives smell of formaldehyde; in heating with sod. salicylate and conc. H_2SO_4 gives methyl salicylate, B. P. 224°, having a characteristic smell.

78° *Ethyl alcohol*, C_2H_5OH—sp 0·789 (20)°, miscible with water: on warming with a solution of iodine and caustic soda yields yellow crystals of iodoform, M P. 119°; heating with $K_2Cr_2O_7+H_2SO_4$ a characteristic odour of CH_3CHO.

97° *N-propyl alcohol*, $CH_3CH_2CH_2OH$—sp. gr 0·804 (20°) miscible with water ; on oxidn. with $K_2Cr_2O_7+H_2SO_4$ gives propionic aldehyde, B. P. 49°; acetate, B. P. 101°.

116° *N-butyl alcohol*, $CH_3CH_2CH_2CH_2OH$—sp. gr. 0·810 (20°), soluble in 11 parts of water; on oxidn. with $K_2Cr_2O_7+H_2SO_4$ yields butyric aldehyde, B. P. 74°; acetate, B. P. 126°.

197° *Ethylene glycol*, $CH_2OH—CH_2OH$ sp. gr. 1·125 (0°), miscible with water; diacetate, B. P. 187°; heat with $KHSO_4$—smell of CH_3CHO is obtained.

205° *Benzyl alcohol*, $C_6H_5CH_2OH$—sp. gr. 1.043 (20°), soluble in 25 parts of water; oxidn. with acid $KMnO_4$ yields benzoic acid, M. P. 121°.

290° *Glycerol*, CH_2OH. $CHOH$. CH_2OH-M. P. 20°, sp. gr. 1·26, miscible with water, sweet taste; on heating with $KHSO_4$ yields acrolein with characteristic odour; triacetate, B. P. 258°; gives Dunstan's test.

ALDEHYDES AND KETONES

Liquids

B. P.

21° *Acetaldehyde*, CH_3CHO—sp. gr. 0.806 (0°), miscible with water, a characteristic odour; reduces Fehling's solution, and restores the colour Schiff s reagent; reduces ammoniacal $AgNO_3$; on heating with alkali, it gives an offensive buggy odour, forming a yellow resin.;

56° *Acetone*, CH_3COCH_3— sp. gr. 0·819 (0°), inflammable liquid, miscible with water; yields iodoform on warming with iodine solution and alkali, M. P. 119°; gives iodoform with ammonia also (distinction from C_2H_5OH); gives a violet colour on shaking with ammonia and a freshly prepared solution of sodium nitroprusside.

80° *Methyl ethyl ketone*, $CH_3COC_2H_5$—sp. gr. 0·839 (0°), miscible with water; yields semicarbazone, M. P. 139°.

98° *Formaldehyde*—(HCHO in aqueous solution.)—a pungent and characteristic odour; aqueous solution on evaporation gives a white solid residue of paraformaldehyde; reduces Fehling's solution;, and restores the colour of Schiff's reagent, does not give offensive odour on heating with alkali (distinction form CH_3CHO).

179° *Benzaldehyde*, C_6H_5CHO—sp. gr. 1·05 (15°), smell of oil of bitter almonds; sparingly soluble in water. Reduces ammoniacal $AgNO_3$ but not Fehling's solution. On oxidation with alkaline $KMnO_4$ gives benzoic acid, M.P. 121°; phenylhydrazone, M. P. 158°.

202° *Acetophenone*, $C_6H_5COCH_3$—M. P. 20°; sp. gr. 1·023 (25°), sparingly soluble in water; on oxidation with alk. $KMnO_4$ gives benzoic acid; phenylhydrazone. M. P., 105°.

PHENOLS

B. P.

181° *Phenol*, C_6H_5OH—M. P. 42°, forms colourless crystals; gives violet colour with $FeCl_3$ in water; a characteristic odour; gives Liebermann's test; with bromine water gives tribromophenol, M. P. 93°; picrate, M. P. 83°.

190° *Ortho-cresol*, $CH_3 . C_6H_5OH$ (1 : 2)—M. P. 31°, violet colour with $FeCl_3$ in water; with bromine water yields dibromo-derivative, M. P. 56°; picrate, M. P. 88°.

201° *Para-cresol*, $CH_3C_6H_4OH$ (1 : 4)—M. P. 35°, blue colour with $FeCl_3$ in water. With excess of bromine water, yields tetrabromo-derivative, M. P. 108°; gives no picrate.

Solids

M. P.

94° *a-Naphthol*, $C_{10}H_7OH$ (1)—no colour with $FeCl_3$ in water but gives a white ppt.; acetate, M.P. 46°; picrate, M. P. 189°.

118° *Resorcinol*, $C_6H_4(OH)_2$ (1: 3)—aq. solution. gives blue violet colour with $FeCl_3$; gives fluorescein test wih phthalic acid. On nitration gives trinitro-derivative, M. P. 175°.

122° *β-naphthol*, $C_{10}H_7OH$ (2)—insoluble in water; no colour with $FeCl_3$ in water but a white opalescence; gives yellow colour with NaOBr; acetate, M. P. 70°; picrate, M. P. 156°.

133° *Pyrogallol*, $C_6H_3(OH)_3$ (1 : 2: 3)—soluble in water; dull yellow colour with $FeCl_3$; soln. in NaOH turns brown in air; blue ppt. with $FeSO_4$ solution. Triacetate, M. P. 161°.

169° *Hydroquinone*, $C_6H_4(OH)_2$ (1 : 4)—soluble in water; a transient blue colour with $FeCl_3$ in water; ammonia colours aqueous soln. brown; diacetate, M. P. 123°: with ferric alum in cold yields quinhydrone, M. P. 171°.

ACIDS

Liquids

B. P.

100° *Formic acid*, HCOOH—M. P. 8°, sp. gr. 1·245 (0°). miscible with water, a characteristic sharp odour, neutral solution of formate gives red colour with $FeCl_3$ solution; reduces mercuric chloride and silver nitrate, ammonium salt, M. P. 114°.

118° *Acetic acid*, CH_3COOH—M. P. 16°, gr. 1·054 (16°): a characteristic odour, miscible with water, neutral solution gives red colour with $FeCl_3$; does not reduce $HgCl_2$ or $AgNO_3$ (distinction from formate); amide, M. P. 82°; ammonium salt. M. P. 66°.

Solids

M. P.

100° *Citrtc acid*, $CH_2COOH. C.(OH) COOH, CH_2COOH, H_2O$—soluble in water; neutral solution gives a white ppt. with $CaCl_2$ *only on boiling*; acetyl derivative, M. P. 115°,

101° *Oxalic acid*, COOH. COOH, $2H_2O$—soluble in water; immediate white ppt. with $CaCl_2$ *in cold*, insoluble in CH_3COOH; anilide M. P. 245°. On heating with conc. H_2SO_4 yields $CO+CO_2$.

121° *Benzoic acid*, C_6H_5 COOH—soluble in hot water; a buff ppt. reddish-brown colour is obtained on adding $FeCl_3$ to neutral solution; amide M. P. 128°. On nitration, m-nitrobenzoic acid, M. P. 140°.

155° *Salicylic acid*, C_6H_4 (OH) COOH, (1 : 2)—a transient violet colour with $FeCl_3$ which changes to purple; a sweet smell of oil of winter green is obtained on heating it with CH_3OH and a drop of conc. H_2SO_4; acetyl derivat., M. P. 135°.

169° *Tartaric acid* $[CH(OH) COOH]_2$—soluble in water; neutral solution gives a white ppt. with $CaCl_2$ *on shaking*; gives a silver mirror with ammoniacal $AgNO_3$; diacetyl derivat., M. P. 58°.

185° *Succinic acid*, $[CH_2COOH]_2$—soluble in water; neutral solution gives a white ppt. on warming with $CaCl_2$ and a reddish-brown ppt. with $FeCl_3$ in cold; gives fluorescein test with resorcinol; on heating gives anhydride, with a penetrating choking smell.

195° *Phthalic acid*, $C_6H_4(COOH)_2$(1:2)—insoluble in water; neutral solution gives no ppt. with $CaCl_2$ but a buff ppt. with $FeCl_3$; gives fluorescein test with resorcinol.

ESTERS

Liquids

B. P.

77° *Ethyl acetate*, $CH_3COOC_2H_5$—sp. gr. 0·924 (0°); on hydrolysis gives ethyl alcohol and acetic acid.

186° *Ethy oxalate*, $(COOC_2H_5)_2$—sp. gr. 1·103 (0°); on hydrolysis gives ethyl alcohol and oxalic acid.

186° *Phenyl oxalate*, $(COOC_6H_5)_2$—sp. gr. 1·081 (15°); on hydrolysis gives phenol and oxalic acid.

213° *Ethyl benzoate*, $C_6H_5COOC_2H_5$—sp. gr. 1·066 (0°); on hydrolysis gives ethyl alcohol and benzoic acid.

224° *Methyl salicylate*, $OH.C_6H_4COOCH_3$—sp. gr.1.199 (4°); odour of oil of winter green; on hydrolysis gives methyl alcohol and salicylic acid.

Solids

M. P.

51° *Methyl oxalate*, $[COOCH_3]_2$—B. P. 163°; on hydrolysis gives methyl alcohol and oxalic acid.

68° *Phenyl benzoate*, $C_6H_5COOC_6H_5$—B.P. 299°; on hydrolysis yields phenol and benzoic acid.

CARBOHYDRATES

Solids

M. P.

146° *Glucose*, $C_6H_{12}O_6$—reduces Fehling's solution; gives silver mirror with ammoniacal $AgNO_3$; on heating with NaOH, the aqueous solution gives yellow colour; osazone, M. P. 205°.

106° *Cane sugar*, $C_{12}H_{22}O_{11}$—does not reduce Fehling's solution but does so only after hydrolysis; charred with conc. H_2SO_4.

Decomposes Starch—insoluble in cold water but dissolves in boiling water; gives a blue colour with weak iodine soln.

B. Compounds containing nitrogen

AMINES

Liquids

B. P.

183° Aniline $C_6H_5NH_2$—sp. gr. 1·027 (17°), not miscible with water; gives an azo dye with α or β naphthol; on warming with alc. KOH and $CHCl_3$ yields phenyl isocyanide; with bromine water yields ppt. of tribromoaniline, M. P. 118°.

193° *Dimethylaniline*, $C_6H_5N\ (CH_3)_2$—(M.P. 2 5°) sp. gr. 0·985 (20°). Hydrochloride (deliques.). M. P. 85-95°; on treatment with $NaNO_2$ in cold gives yellow oily nitroso-compound, M. P. 85°; picrate, M. P. 163°; gives azo dyes with diazotised p-amines.

197° *o-Toluidine*, $CH_3C_6H_4\ NH_2$ (1:2)—sp. gr. 1·003 (20°), not miscible with water; solution in 50% H_2SO_4 gives blue colour with $K_2Cr_2O_7$ which changes to purple on dilution; acetyl derivative, M. P. 112°; gives an azo dye when diazotised and cooled with α- or β-naphthol.

Solids

M. P.

45° *p-Toluidine*, $CH_3C_6H_4NH_2$ (1:4)—(B.P. 200°) almost insoluble in water; the hydrochloride when diazotised and coupled with α- or β-naphthol gives an axo dye; solution in 50% H_2SO_4 gives yellow colour with $K_2Cr_2O_7$; acetyl derivative, M. P. 148°.

50° α-Naphthylamine, $C_{10}H_7NH_2$ (1)—bad odour; the solution of hydrochloride gives a blue ppt. with $FeCl_3$; the hydrochloride when diazotised and coupled w th α-or β-naphthol gives an azo dye; acetyl derivative, M. P. 159°; picrate, M. P. 161°.

111° *β-Naphthylamine*, $C_{10}H_7NH_2$ (2)—odourless; no colour with $FeCl_3$; gives azo dye as other p-amines; acetyl derivative, M. P. 132°; picrate, M. P. 195°.

AMIDES AND ANILIDES

Solids

M. P.

82° *Acetamide*, CH_3 $CONH_2$—on heating with strong alkali gives ammonia and pot. acetate; picrate. M. P. 107°.

114° *Acetanilide*, $CH_3CO.\ NHC_6H_5$—on hydrolysis gives aniline and CH_3COOH; with bromine in acetic acid gives p-bromoderivative, M. P. 16·7°.

128° *Benzamide*, $C_6H_5CONH_2$—on hydrolysis gives ammonia and benzoic acid; with aniline yields benzanilide, M. P. 160°.

132° *Urea* (*carbamide*), $H_2N.\ CO.\ NH_2$—gives smell of ammonia on heating in a dry test tube; the residue gives biuret test; with HNO_3 gives nitrate, M. P. 163°.

Nitro Compounds

Liquids

B. P.

210° *Nitrobenzene*, $C_6H_5NO_2$—M. P. 5°, sp. gr. 1·197 (25°); odour of oil of bitter almonds; on reduction with Sn and HCl, yields aniline; on warming with fuming $HNO_3+H_2SO_4$ yields m-dinitrobenzene, M. P. 90°.

220° *o-Nitrotoluene*, $CH_3.\ C_6H_4.\ NO_2$ (1:2)—sp. gr. 1·162 (20)°; odour like nitrobenzene; on reduction gives o-toluidine; on oxidation with alk. $KMnO_4$, gives o-nitrobenzoic acid, M. P. 147°.

230° *m-Nitrotoluene*, $CH_3.\ C_6H_4.\ NO_2$ (1:3)—M. P. 16°, sp. gr. 1·16 (17°), resembles o-nitrotoluene; on oxidation gives m-nitrobenzoic acid, M. P. 146°.

solids

M. P.

44° *o-Nitrophenol*, NO_2 $C_6H_4.$ OH. (1:2)—B. P. 215°, bright yellow, with a characteristic odour; soluble in dil. NaOH with orange colour; acetyl derivative M. P. 40°.

61° *a-Nitronaphthalene*, $C_{10}H_7 . NO_2$ (1)—forms dark red solution in conc. H_2SO_4; on reduction with Sn+HCl gives *a*-naphthylamine, M. P. 50°.

90° *m-Dinitrobenzene* $C_6H_4 . (NO_2)_2$ (1 :3)—light yellow; on adding a trace of $SnCl_2$ to its solution in dil. NaOH (boiling) gives violet colour.

114° *p-Nitrophenol*, $OH. C_6H_4 . NO_2$ (1:4)—colourless, soluble in dil. NaOH with bright yellow colour, acetyl derivative, M. P. 81°.

C. Compounds containing chlorine

Liquids

B. P.

61° *Chloroform*, $CHCl_3$—sp. gr. 1·504 (12°); reduces Fehling's solution; insoluble in water, gives emulsion; on warming with aniline and alc. KOH gives phenyl isocyanide; gives red colour on warming with resorcinol and dil. NaOH.

78° *Carbon tetrachloride*, CCl_4—sp. gr. 1·608 (10°); characteristic odour.

83° *Ethylene chloride*, $CH_2 Cl. CH_2 Cl$—sp. gr. 1·252 (20°). on prolonged heating with aniline yields a product, M. P. 163°.

132° *Chlorobenzene*, C_6H_5Cl—sp. gr. 1·107 (20°); on warming with a mixture of nitric acid and sulphuric acid to about 85° gives 2:4 dinitro-derivative, M. P. 52°.

Solids

M. P.

53° *p-Dichlorobenzene*, $C_6H_4Cl_2$ (1:4)—B. P. 172°; on nitration with conc. HNO_3 and H_4SO_4 yields 2:5 dichlorodinitrobenzene M. P. 54°.

57 *Chloral hydrate*, $CCl_3 . CH(OH)_2$—reduces Fehling's solution; on heating with alkali gives chloroform.

D. Compounds containing bromine

Liquids

B. P.

38° *Ethyl bromide*, C_2H_5 Br.—sp. gr. 1·45 (15°).

157° *Bromobenzene*, C_6H_5Br.—sp. gr. 1·49 (20°) with $HNO_3 + H_2SO_4$ at 90° yields 2:4 dinitrobromobenzene, M. P. 75°.

Solids

M. P.

89° *p-Dibromobenzene*, C_6H_4 Br_2 (1:4)—B. P. 219°, on nitration yields 2:5 dibromodinitro benzene, M. P. 84°.

E. Compounds containing iodine

Liquids

M. P.

119° *Iodoform*, CHI_3—yellow with a chracteristic odour: gives red colour on warming with phenol in dil. alc. NaOH.

PART VIII

Some Typical Organic Preparations

1. Ethyl Iodide, C_2H_5I.

Reaction—It is obtained by the action of red phosphorus and iodine on absolute alcohol:

$$5C_2H_5OH + P + 5I = 5C_2H_5I + H_3PO_4 + H_2O$$

If *yellow* phosphorus is used, the reaction is sometimes represented as:

$$PI_3 + 3C_2H_5OH = 3C_2H_5I + P(OH)_3.$$

Reactants:

30 g. Absolute alcohol.
75 g. Iodine.
6 g. Red phosphorus.

Preparation—Take a flask of 300 ml. capacity. Place the whole quantity of phosphorus in it and then add alcohol to it. Add the whole iodine in 10 instalments at the interval of 12 minutes each. Shake the flask from time to time and cool under a tap. Allow it to stand further for about three hours and then heat with a reflux condenser over a water bath for an hour.

Now pour the contents in a distillation flask, and distil over a water bath. The distillate would consist of ethyl iodide, alcohol and traces of iodine. Transfer the distillate to a separating funnel and shake it with dilute caustic soda solution, till the mixture is colourless. Separate the lower layer which consists of ethyl iodide. Allow it to stand along with a few pieces of fused calcium chloride for half-an-hour and redistil the contents on a water bath.

Yield—about 60 g., b. p. 72°, sp. gr. 1·94 at 15°.

Alternate Method

2 g. of *yellow* phosphorus (weighed under water, cut into small pieces, and dried with filter paper) are added gradually to the theoretical amount of iodine contained in a 250 ml. round-bottomed flask. The flask is attached to a reflux condenser, and and cooled. 25 ml. (excess) of absolute alcohol are added gradually at this stage through the condenser tube. After the vigorous reaction has subsided, the flask is heated on a water bath with occasional shaking, until all the phosphorus iodide has been decomposed (1.5—2 hrs.) The ethyl iodide is then distilled off in the usual manner, either by immersing the flask in the boiling-water bath or by heating on a sand bath. The distillate is freed from alcohol by washing several times with water. In case it is coloured brown by iodine, it is again shaken with water to which a few drops of sodium hydroxide solution have been added. It is then dried over granular calcium chloride, decanted into a distilling flask and re-distilled. Yield—28 g.

2. Ethyl ether, $C_2H_5O.\ C_2H_5$.

Reaction—It is obtained by the action of concentrated sulphuric acid on ethyl alcohol.

$$2C_2H_5OH = C_2H_5.\ O.\ C_2H_5 + H_2O$$

The acid acts as a dehydrating agent.

Reactants—

75 g. Concentrated sulphuric acid.

75 g. Ethyl alcohol (should not contain more than 10% water).

Preparation—Take a half-litre capacity distilling flask. In the flask introduce the whole sulphuric acid and half the quantity of alcohol (30-50) g. Fit up the flask with a tap funnel and a thermometer, and connect it with a condenser. Fit the end of the latter into a distillation flask, the side-tube of which is connected with a piece of rubber tubing leading over the edge of the working table, so that the uncondensed ether vapour does not catch fire. As soon as the temperature of the liquid rises to 140°, ether begins to distil over. Alcohol is now added from the tap funnel at about the same rate at which the ether distils over, and the temperature is kept within 140-145°. Tap funnel should dip below the surface of the liquid.

Ether collected in the receiver is mixed with alcohol and water (and also sulphur dioxide). Transfer it to a separating funnel and shake it with caustic soda solution. Separate the non-aqueous layer and dry it in contact with fused calcium chloride. Again distil

the ether on a previously warmed water-bath when the whole should pass over between 34°-46°.

Ether has b. p. 35°, sp. gr. 0.72 at 15°.

Acetaldehyde, CH_3CHO.

Reaction—It is obtained by the oxidation of absolute alcohol by potassium dichromate and concentrated sulphuric acid :

$$K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O.$$
$$CH_3CH_2OH+O=CH_3CHO+H_2O.$$

40 g. Potassium dichromate.

160 ml. Water.

45 ml. Ethyl alcohol.

25 ml. Concentrated sulphuric acid.

Preparation—Place coarsely powdered potassium dichromate and water in a litre flask fitted with a tap funnel and attached to a condenser. Heat the flask gently on a water-bath. Now add drop by drop a mixture of alcohol and concentrated sulphuric acid and shake the flask almost continuously during the operation. A vigorous reaction sets in. Collect the distillate in the receiver which consists of aldehyde, alcohol, acetal and water.

Redistil the contents of the receiver fractionally from a water bath. Fit up the condenser in a way that it is inclined upwards and by means of the siphon and rubber tubing is filled with water at 25° from a vessel. The flow of water is controlled by a screw pinch-cock.

In the condenser, are condensed alcohol and water vapours which flow back into the distillation flask, and the aldehyde vapours over to the receiver. The receiver is cooled in ice. Acetaldehyde collected in the receiver is cooled in ice. Acetaldehyde collected in the receiver may again be subjected to fractional distillation, and the portion distilled between 20-22° collected. It consists of pure acetaldehyde.

In case it is desired to prepare aldehyde-ammonia, the aldehyde is collected in dry ether placed in the receiver and cooled with ice. Aldehyde is absorbed in ether: a current of dry ammonia is passed, and the crystals of aldehyde-ammonia collected. Filter them at the pump, wash with ether and dry on a filter paper.

Aldehyde-ammonia again gives the pure aldehyde distilled with dilute sulphuric acid.

In the Indian laboratories, where the temperature is usually above 22°, one ought to be satisfied with the preparation of aldehyde-ammonia, and should not attempt at preparing pure aldehyde.

Yield—8 g. of aldehyde-ammonia.

Alternate Method

25 g. calcium acetate and 25 g. of calcium formate are well mixed and heated in a hard glass round bottomed flask, fitted with a long condenser. The end of the condenser tube is fitted with an adapter, which leads into a receiver surrounded by a freezing mixture of ice and salt. The acetaldehyde is distilled over. This may be converted to aldehyde-ammonia.

$$(CH_3COO)_2Ca+(HCOO)_2Ca=2CH_3CHO+2CaCO_3.$$

4. Acetone, CH_3COCH_3.

Reaction—Acetone is prepared by heating dry calcium acetate :

$$(CH_3COO)_2Ca=CH_3COCH_3+CaCO_3.$$

Preparation—By means of a large luminous flame kept in constant motion, heat about 50 g. of dry calcium acetate in a retort or a distillation flask connected with a long condenser. Heat gently at first and then strongly. A light brown liquid distils over consisting of acetone and a little tarry matter.

Shake the distillate with a saturated solution of sodium bisulphite, slightly warm it and allow it to cool. Crystals of acetone-sodium bisulphite are obtained. Separate them at a filter-pump, press between the folds of a filler paper and distil them with sodium carbonate solution (saturated). Dehydrate acetone over fused calcium chloride.

acetone acetone-bisulphite

$$2(CH_3)_2C(OH)SO_3Na+Na_2CO_3$$
$$=2CH_3COCH_3+2Na_2SO_3+CO_2+H_2O$$

Pure acetone is a colourless mobile liquid, b. p. 56·5°; sp. gr. 0·777 at 15°.

Acetamide, CH_3CONH_2.

Reaction—This is obtained by distilling ammonium acetate :

$$CH_3COONH_4=CH_3CONH_2+H_2O.$$

Ammonium acetate—For its preparation, take 50 g. of glacial acetic acid into a large evaporating basin, and warm it gently on a hot water bath. Neutralise the acid by gradually adding finely powdered ammonium carbonate (70 g.) with constant stirring (till a test portion shows alkaline reaction towards litmus). The mixture is then heated on the water bath until another test portion shows an *acid* reaction. The contents are then cooled, and the crystals of ammonium acetate pressed between filter papers.

Preparation—Take 50 g. of ammonium acetate in a porcelain dish and heat it till it melts. Pour the molten mass in the distillation flask fitted with air condenser and a thermometer. Start the distillation on a sand bath. The distillate consists of ammonia, water, and acetic acid, and when the temperature approaches 180°, the molten mass solidifies. It now mainly consists of acetamide. Transfer the distillate again into the distillation flask and repeat the distillation. When a sufficient amount of acetamide has been collected, take it out and dry it on a porous plate or between the folds of a filter paper. It may be recrystallised from ether.

A better yield is obtained if the distillation is carried under high pressure and at 200°.

M. P. 82°; b. p. 223°.

6. **Formic acid,** HCOOH.

Reaction—It is obtained by the action of glycerine on oxalic acid; at first mono-oxalin is formed, which then loses a molecule of carbon dioxide forming monoformin. The monoformin on hydrolysis yields formic acid and glycerine.

$$CH_2OH(CHOH)CH_2OH + HOOC.\ COOH$$
$$= \underset{\text{mono-oxalin.}}{CH_2OH(CHOH)\ CH_2O.\ CO.\ COOH} + H_2O.$$

$$CH_2OHCHOHCH_2.\ O.\ CO.\ COOH$$
$$= \underset{\text{monoformin}}{CH_2OH(CHOH)\ CH_2O.\ CO.\ H} + CO_2$$

$$CH_2OH(CHOH)\ CH_2O.\ CO.H + H_2O$$
$$= \underset{\text{glycerine}}{CH_2OH(CHOH)\ CH_2OH} + \underset{\text{formic acid.}}{HCOOH.}$$

Reactants—

60 g. Glycerine.

125 g. Crystallised oxalic acid.

Preparation—Glycerine is placed in a retort with thermometer and connected with a condenser. Add to it about 60 g. of the

crystallised oxalic acid and heat the mixture to 100-110° on a sand-bath; a little below this temperature, the evolution of carbon dioxide commences, and dilute formic acid distils over. But after sometime the action ceases. Add at this stage the remaining quantity of oxalic acid, and maintain the previous temperature (100-110°). Carbon dioxide is again evolved, and a more concentrated formic acid distils over in the receiver. Repeat the process with further quantities of oxalic acid.

Neutralise the acid with lead carbonate, and heat; filter hot and cool. This would yield lead formate crystals. They may be dried and decomposed with hydrogen sulphide to recover pure formic acid, which may be distilled over.

$$(HCOO)_2\ Pb + H_2S = 2HCOOH + PbS.$$

Yield is theoretical, b. p. 100°; sp. gr. 1·21 at 20°.

7. **Chloroform.** $CHCl_3$.

Reaction—It is obtained by the action of bleaching powder on alcohol; the alcohol is first oxidised to aldehyde which is subsequently chlorinated to yield chloral; this is then hydrolysed to chloroform. All these reactions proceed almost simultaneously :

$$CH_3CH_2OH + CaOCl = CH_3CHO + CaCl_2 + H_2O.$$
$$2CH_3CHO + 6CaOCl = 2CCl_3CHO + 3Ca(OH)_2 + 3CaCl_2.$$
$$2CCl_3CHO + Ca(OH)_2 = 2CHCl_3 + (HCOO)_2Ca.$$

Reactants—

100 g. Bleaching powder.
25 ml. Absolute alcohol.
250 ml. Water.

Preparation—Take the whole of the bleaching powder in a mortar and grind it to a cream with 150 ml. of water. Transfer it to a flask of $1\frac{1}{2}$ litre capacity. Add rest of the water also to the flask and transfer the whole alcohol also. Place the flask on waterbath and attach it with a condenser. Heat gently till the reaction commences, and then remove the burner. Heat of the reaction is sufficient to distil over the chloroform now. See that frothing does not go out of control. When the reaction slackens, the contents may again be heated to complete the distillation.

Transfer the distillate to a separating funnel and shake it with alkali solution. The lower layer of chloroform is then tapped off. The liquid is then dried over fused calcium chloride and redistilled.

Yield—25 g., b. p. 60·6°, sp. gr. 1·5.

8. Iodoform, CHI_3.

Reaction—It is obtained by the action of iodine on acetone in presence of sodium carbonate.

$$CH_3COCH_3+6I+3Na_2CO_3=2CHI_3+6NaI+2H_2O+4CO_2$$

Reactions—

15 ml. Acetone.

15 g. Sodium carbonate crystals; dissolve in 80 ml. of water.

8 g. iodine.

Preparation—Mix the sodium carbonate solution with acetone and keep the mixture in a water-bath maintained at 75° Add with constant stirring the whole amount of iodine, in several instalments. Allow the mixture to stand for sometime. When the iodine colour has disappeared, allow the mixture to cool slowly. The yellow crystals of iodoform would gradually settle down. Filter them and wash with cold water. Dry them over a porous plate or between the folds of a filter paper.

Yield—10 g., m. p. 119°.

N. B.—Iodoform may also be similarly prepared from rectified spirit [take 15 ml. of rectified spirit instead of 15 ml. of acetone.].

9. Nitrobenzene, $C_6H_5NO_2$.

Reaction—It is obtained by the action of concentrated nitric acid on benzene in presence of concentrated sulphuric acid :

$$C_6H_6+HNO_3=C_6H_5NO_2+H_2O$$

Reactants—

50 ml. (50 g.) Benzene.

50 ml. (55 g.) Concentrated nitric acid, sp. gr. 1·456.

80 ml. (72 g.) Concentrated sulphuric acid, sp. gr. 1·842.

Preparation—Take benzene in a half-litre flask. Prepare the mixture of nitric and sulphuric acids in another flask. Add the mixture in small quantities at a time to the benzene, and shake the contents after each addition, and cool the flask under tap. (Maintain the temperature below 40° all while). Keep the mixture now for about an hour in a bath maintained at 50-60°, and shake the flask from time to time. Now cool the flask and pour the contents in 5-10 volumes of water. Separate the nitrobenzene layer with a tap-funnel. Wash the oily layer with dilute solution of caustic soda, and then with water, and finally dry it over anhydrous

calcium chloride. Redistil the nitrobenzene and collect the distillate boiling between 204-207°.

Yield—60 g., b. p. 209°, sp. gr. 1·21.

10. Meta dinitrobenzene, $C_6H_4(NO_2)_2$

Reaction—It is obtained by the action of fuming nitric acid on nitrobenzene in presence of concentrated sulphuric acid.

$$C_6H_5NO_2 + HNO_3 = C_6H_4(NO_2)_2 + H_2O.$$

Reactants—

20 g. Nitrobenzene.
25 g. Fuming nitric acid, sp. gr. 1·5.
40 g. Concentrated sulphuric acid.

Preparation—Place in the reaction flask the mixture of nitric and sulphuric acids carefully prepared. Run into it gradually the nitrobenzene with constant shaking. Place some unglazed procelain pieces in the flask, and heat the contents on a sand-bath until a sample of the contents poured in cold water solidifies (a drop of the oil may be tested with cold water). About half an hour is required for the reaction. Now cool the mixture and pour the contents in about 250 ml. of water. Now separate the yellow solid by filtration, wash it with water and recrystallise from hot alcohol on a water-bath. Allow the solution to stand for a few hours, and separate the crystals and dry them over a porous plate.

Yield—24 g., m.p. 90°. Pale-yellow flat needles.

11. Aniline, $C_6H_5NH_2$.

Reaction—It is obtained by the action of tin and hydrochloric acid on nitrobenzene.

$$2C_6H_5NO_2 + 3Sn + 12HCl = 2C_6H_5NH_2 + 3SnCl_4 + 4H_2O.$$

Reaction—

20 g. Nitrobenzene.
40 g. Granulated tin.
100 ml. Concentrated hydrochloric acid, sp. gr. 1·16.

Preparation—Place tin and nitrobenzene in a flask of 1 litre capacity, and add to the contents concentrated hydrochloric acid, small portions at a time with frequent stirring. The vigour of reaction may be controlled by placing the flask in cold water from time to time. The reaction is complete when there is no more

of the nitrobenzene smell. Now on cooling, aniline stannichloride, $(C_6H_5NH_2, HCl)\ SnCl_4$, begins to crystallise. A cold solution of caustic soda (75 g.) in water (100 ml.) is added very carefully in small quantities at a time, the flask being shaken well. Aniline is liberated, the layer of which is separated by a tap-funnel. It is then subjected to steam distillation (or may be extracted with ether). The distillate is saturated with salt, and the base is separated, dried over solid potash, decanted into a dry flask and further purified by distillation.

B. p. 184°, sp. gr. 1·1026 at 15°.

12. **Sulphanilic** Acid, $C_6H_4(NH_2)SO_3H$.

Reaction—Sulphanilic acid or para-amino-benzene sulphonic acid is prepared by sulphonation of aniline.

$$2C_6H_5NH_2 + H_2SO_4 \rightarrow (C_6H_5NH_2)_2H_2SO_4$$

$$C_6H_5NH_2)_2H_2SO_4 + H_2SO_4 = 2C_6H_5NHSO_3H + 2H_2O.$$
$$= 2NH_2.C_4H_4.SO_3H + 2H_2O.$$

Reactants—

10·2 g. aniline

37 g. conc. H_2SO_4

Preparation—Take 10·2 g. (10 ml.) of aniline in a conical or or round-bottomed flask and carefully add 37 g. (20 ml.) of concentrated sulphuric acid in small portions. While adding the acid, the contents of the flask are to be gently swirled, and cooled in a cold bath. When the whole of the acid has been added, heat the contents on an oil bath for about 5 hours at 180°—190°. The sulphonation is supposed to be complete when a test portion (2 drops) is completely dissolved by 3-4 ml. of 2 *N*-NaOH solution. When the reaction is found thus to be complete, the contents of the flask are poured with stirring into 200 g. of ice-cold water and allowed to stand for 10 minutes. The precipitated sulphanilic acid is filtered, and washed with water.

The crude acid thus obtained is dissolved in boiling water and treated with animal charcoal filtered hot and recrystallised. Yield is about 10 g.

13. **Acetanilide,** $C_6H_5NH.CO.\ CH_3$

Reaction—Acetanilide is prepared by the acetylation of the amino group of aniline.

$$2C_6H_5NH_2 + (CH_3CO)_2O = 2C_6H_5NH.\ COCH_3 + H_2O.$$

Reactants—

10·25 g. aniline in 10 ml. conc. HCl.

14·0 g. acetic anhydride.

17·0 g. Na-acetate.

Preparation—In a flask add 10 ml. of conc. hydrochloric acid to 250 ml. of water, and then mix 10.25 g. of aniline. On shaking, aniline will pass into solution. Add to the mixture 14 g. of acetic anhydride, stir well until it is dissolved and then, immediately pour in a solution of 16 g. of sodium acetate dissolved in 50 ml. of water. The contents are vigorously stirred and cooled in ice. Acetanilide crystals are filtered under suction, washed with a small quantity of water, and dried on filter paper in air.

The substance is recrystallised from 250 ml. of boiling water to which 5 ml. of methylated spirit have been added.

Yield—14 g., M. P. 114°.

14. Diazobenzene chloride, $C_6H_5N:NCl$

Reactions—It is obtained by the action of nitrous acid (from amyl nitrite and hydrochloric acid) on aniline in presence of concentrated hydrochloric acid.

$$C_6H_5NH_2+ON.OH+HCl=C_6H_5N:NCl+2H_2O.$$

Reactants—

15 g. Aniline.

150 ml. Absolute alcohol.

75 g. Concentrated hydrochloric acid.

24 g. Amyl nitrite.

Preparation—Dissolve aniline in alcohol and add to the solution concentrated hydrochloric acid in a slow stream and shake contantly. The precipitate of the hydrochloride appears which dissolves later on. Cool the mixture to about 20°, agitate it and add amyl nitrite in small amounts at a time from a tap-funnel. Now bring down the temperature to 10° by placing in ice mixture. Crystals of diazobenzene chloride will separate out, which may be filtered at the pump and washed with alcohol, and ether and dried in air at the ordinary temperature. (Drying is always inadvisable, as the substance decomposes with explosion. The substance is used for further reactions in the state of solution).

Alternate Method

10 g. of aniline (1 mol.) are dissolved in 50 ml. of a mixture of equal volumes of concentrated hydrochloric acid and water (more

than 2 mols.) and the mixture is very well cooled in ice. Now 8·9 g. of sodium nitrite (more than 1 mol.), dissolved in 20 ml. of water, are then added solwly from a dropping funnel, the end of which dips under the solution of aniline. The mixture is kept well agitated during the addition and the temperature is not allowed to rise. The addition of the nitrite solution is continued until a drop of the mixture, withdrawn by means of a glass rod, indicates the presence of free nitrous acid by giving a blue colouration with starch-potassium iodide paper.

The solution of the diazonium salt prepared in this way may be used for various other preparations.

15. Azobenzene $C_6H_5N:NC_6H_5$

Reaction—It is obtained by the action of iron filings on azoxybenzene.

$$C_6H_5N(O)NC_6H_5+Fe=C_6H_5N:NC_6H_5+FeO.$$

Reactants—

10 g. Azoxybenzene.

30 g. Iron filings.

Iron filings are freed from oil by washing them with alcohol and ether and finally dried in the steam oven.

Preparation—Grind azoxybenzene and iron filings to a fine powder, and place the mixture in a hard glass wide tube sealed at one end and drawn at right angles at the other (a retort may instead be used). The drawn end dips into a receiver which may be a beaker. Heat the tube gradually to a high temperature (340°); the azobenzene distils over as an oil which solidifies to a bright red crystalline mass as soon as it cools. Wash it with dilute hydrochloric acid and then with water. Dry the residue on a porous plate. It may be recrystallised from petroleum ether.

M. p. 61°: b. p. 293°.

16. Phenol, C_6H_5OH

Reaction—It is obtained by heating diazobenzene sulphate (obtained by reacting aniline with amyl nitrite and concentrated sulphuric acid) with water.

$$(C_6H_5N:N)_2SO_4+2HOH=2C_6H_5OH+2N_2+H_2SO_4$$

Reactants—

7·5 g. Aniline.

75 g. Absolute alcohol.

20 ml. Concentrated sulphuric acid.

10 ml. Amyl nitrite.

Preparation—Aniline and alcohol are dissolved together To the solution, add concentrated sulphuric acid with constant stirring. Maintain the temperature near about 25° and add amyl nitrite in small amounts at a time, and shake continuously . Add a few drops of ether and allow the mixture to stand for 25 minutes. Filter off the diazobenzene sulphate and wash it a little with alcohol.

Dissolve the diazonium compound in water and decompose it by boiling (an upright air condenser may be fitted). After a brisk boiling for 25 minutes, carry on the steam distillation. Phenol will volatilise along with steam and will collect in the distillate. Saturate the distillate with common salt, and separate the layers with a tapfunnel. Phenol may be further extracted with ether. The ethereal solution is dried over fused calcium chloride, and ether removed on water-bath. Phenol may be further purified by distillation on a direct flame at about 183°.

B. P. 183°; m. p. 43°.

Alternate Method

10 g. aniline are added to the hot solution obtained by pouring 20 g. of concentrated sulphuric acid into 50 ml. of water. The resulting solution is cooled in ice, and diazotised by adding 8-9 g. of sodium nitrite dissolved in 20 ml. of water. The mixture is kept well agitated in ice.

The diazonium salt thus obtained in the state of solution is heated gently on water bath for half an hour, and then distilled with steam. The distillate is extracted with ether, the ethereal solution dried with fused sodium sulphate and fractionated. The phenol distils over at 183°.

Yield.—6·8 g.; m. p. 43°.

17. Methyl orange, $SO_3H.\ C_6H_4\ N : N.\ C_6H_4N(CH_3)_2$.

Reaction—It is obtained by diazotising sulphanilic acid and then coupling it with dimethyl aniline;

$$SO_3H.C_6H_4NH_2+2NaNO_2+2HCl=SO_3H.\ C_6H_4N:N.Cl+NaCl+2H_2O$$

$$SO_3H.\ C_6H_4N:N.Cl+C_6H_5N(CH_3)_2=SO_3H.C_6H_4N:N.C_6H_4.N(CH_3)_2.$$

Reactants—

5·3 g. Sulphanilic acid $(2H_2O)$,

1·4 g. Anhydrous Na_2CO_3.

1·9 g. Sodium nitrite.
6 g. Hydrochloric acid (conc.).
3·0 g. Dimethylaniline.
1·5 g. Glacial acetic acid.
20% solution of NaOH.

Preparation—In a conical flask, take 5·3 g. of sulphanilic acid and 1·4 g. of sodium carbonate and dissolve in 50 ml. of hot water. Cool the solution in ice water to 5°—10°, and add a solution of 1·9 g. of sodium nitrite in 5 ml. of water. Pour the solution slowly with stirring to 6 g. of conc. hydrochloric acid and 40 g. of crushed ice placed in another beaker. Fine crystals of the diazobenzene sulphonate will separate. Do not filter them.

Dissolve separately 3 g. (or 3 ml.) of dimethyl aniline in 1·5 g. of glacial acetic acid. Add this solution to the diazo-product obtained above in the suspension state and stir vigorously. Allow the contents to stand for 10 minutes. The acid form of the methyl orange will separate out. The acid form is treated with 78 ml. of 20 per cent sodium hydroxide solution. This furnishes orange crystals of methyl orange salt (Na-salt). Boil the contents, add 5 g. of sodium chloride, cool in ice water and filter off methyl orange crystals.

Yield—·6 g.

18. Fluorescein and Eosin

Reaction—When phthalic anhydride is condensed with two mols. of resorcinol in presence of a water-eliminating agent like zinc chloride, we get fluorescein. This when treated with bromine furnishes a tetra-bromo compound, known as eosin.

$$C_6H_4(CO)_2O + 2C_6H_4(OH)_2$$
$$= \underset{\text{fluorescein}}{C_6H_4 : CO(O)C[C_6H_3(OH).O.C_6H_3(OH)]} + 2H_2O.$$
$$\text{Fluorescein} + 4Br_2$$
$$= \underset{\text{eosin}}{C_6H_4 : CO(O)\ C[C_6HBr_2(OH).O.\ C_6HBr_2(OH)]} + 4HBr.$$

Reactants—

(*i*) 7·5 g. Phthalic anhydride.
11 g. Resorcinol.
4 g. Zinc chloride (anhydrous).

(ii) 8 g. Fluorescein.
40 ml. Rectified or methylated spirit.
18 g. (6 ml.) Bromine.

Preparation—Fluorescein—Mix well 7·5 g. of powdered phthalic anhydride and 11 g. of resorcinol and transfer the mixture to a small conical flask (150 ml.). Heat this flask in an oil bath heated to 180°, weigh out 4 g. of fused anhydrous zinc chloride in a stoppered bottle (zinc chloride should be freshly fused in a porcelain dish, and then powdered; it should not be exposed to air). Add zinc chloride to the mixture kept in oil bath in small portions at a time, and stirring is continued with the thermometer placed in the mixture. Continue heating at 180° and stirring simultaneously until the solution becomes so viscous that further stirring is rendered impossible (60 minutes), The resulting dark product consists of fluorescein and zinc salts. Allow the flask to cool to 90°; add 100 ml. of water and 5 ml. of concentrated hydrochloric acid to the reaction mixture, and raise the temperature to the boiling of the contents (110°). When all the zinc salts have gone into the solution, filter the insoluble residue of fluorescein at the pump, grind it with water and filter. Dry it at 100°.

Yield :—15 g.

Eosin—Place 8 g. of the prepared fluorescein and 40 ml. of spirit in a small flask (150 ml.). Support a small dropping funnel or a burette containing 6 ml. (18 g.) of bromine above the flask. *Be very careful in handling bromine and the stop-cock of the funnel or burette should be well lubricated.* Add bromine drop by drop in course of 20 minutes. When half the quantity of bromine has been added, a dibromo compound is formed and all the solid material passes into the alcoholic solution. On further adding bromine, a tetrabromocompound (*i.e.* eosin) separates out (which is sparingly soluble in alcohol). The reaction mixture is then allowed to stand for 2 hours. Eosin in filtered off at the pump, washed with alcohol and dried at 100°.

Yield:—12 g.

PART IX

SOME EXPERIMENTS IN PHYSICAL CHEMISTRY

I. Calibration of Volumetric Apparatus.

For volumetric work, flasks, pipettes and burettes are employed, which are constructed and marked so as to take up or deliver a definite volume of liquid. On the apparatus is marked the temperature and the volume corresponding to it. For ordinary work, these graduations are quite reliable, but there is a possiblity of slight error for every accurate experiments. Thus a ten ml. pipette may be delivering only 9·95 ml. or even 10·05 ml. In ordinary volumetric analysis involving double titrations, the graduation, of course, gives rise to no error, because the volume measurements are only relative. The case is, however, quite different when the volumetric apparatus is to be used for the purpose of preparing solutions of definite concentrations, or for other purposes where the different measures are used independently.

Thus the calibrations are of two types: (i) Relative calibrations, in which a pipette, a burette and a flask is calibrated with respect to each other. This is necessary for titrations and similar experiments. (ii) Independent calibrations in true ml.

The process of relative calibration is easy. A pipette may be regarded as standard. It is filled up with a liquid up to the mark. Some liquid is taken in a burette and the reading taken. Now the liquid from the pipette is poured into the burette, and the reading taken. It is then seen whether the volume delivered from the pipette does exactly correspond to the volume recorded from the burette.

The observed error, if any, is noted. Verification is made for different ranges in the burette in a similar way:

Volume delivered from the pipette	... 10 ml.
First burette reading	... 40
Second burette reading	... 30·15

This shows that 10 ml. of the pipette corresponds to 9·85 divisions on the burette.

The fact is taken into account while the burette readings are used for calculations.

The graduated flask is then calibrated with respect to the already calibrated burette. The flask is completely dried, and filled up with water from a burette. The capacity up to the mark is noted. A 100 ml. flask may thus be actually containing 99·5 or 100·5 ml. of the solution with respect to our calibrated pipette and burette.

The method of *independent calibrations* is given below. In this case, one determines the weight of a liquid, generally water (distilled), required to fill the volume, the weight being reduced to vacuum. To save the trouble of making this reduction, use may be made of the following table :

Temperature	Appt. weight of 1 ml. of water	Volume corresp. to 1 g. of water
15°	0·9981	1·0018
16°	0·9979	1·0021
18°	0·9976	1·0024
20°	0·9972	1·0028
22°	0·9967	1·0033
24°	0·9963	1·0037
26°	0·9959	1·0042
28°	0·9954	1·0047
30°	0·9950	1·0051

which gives the volume (in true ml.) corresponding to an apparent weight of 1 g. of water, and the apparent weight of 1 ml. of water at different temperatures.

Experiment.—*Calibration of a pipette*—Pipettes are calibrated by weighing water which they deliver. The following precautions are observed. In the first place it must be seen that the glass of the pipette is free from all greasiness, so that water runs from the pipette without leaving drops behind. The pipette, therefore, should be thoroughly cleaned. This is best effected by filling the pipette several times with warm concentrated sulphuric acid to which a little potassium dichromate has been added. (Care must be taken not to suck the solution into the mouth). In the second place, attention must be paid to the way in which the pipette is allowed to deliver. The pipette should

usually be held upright, or in any case, not sloping at an angle greater than 45°. and the liquid is allowed to run freely. Immediately the liquid stops running, touch the tip of the pipette against the side of the vessel, so as to remove the drop of the liquid which collects at the tip and then withdraw the pipette.

Take a small stoppered flask and weigh it carefully. Suck in distilled water in the pipette up to the mark and deliver the liquid as described above in the stoppered flask. Now again weigh the stoppered flask. From the weight of water the volume can be calculated by the use of the table given above. If necessary, one can for himself determine the density of water at the temperature and make calculations. The experiment is repeated a number of times and the average taken.

The readings are recorded as below:—

Temperature= (say 24°) Density of water

Pipette used= 10 ml. at this temp.=.

Readings	First weight of the flask	Second weight of the flask	Weight of 10 ml. of water	Correct volume-W/D	Error
1.	25·00 g.	34·8 54 g.	9·8554	$\frac{9·8554}{0·99635}$	
2.					
3.					

Experiment 2—*Calibration of a burette*—Burettes are most simply calibrated with the help of a small pipette, usually 2 ml., already calibrated by the method given above. Or, it may be calibrated by the method already described for calibrating pipettes.

Clean burette with chromic acid solution (potassium dichromate and strong sulphuric acid), and finally clean it with water. Clamp it in an exact vertical position and fill it up with distilled water up to a certain level. Weigh a stoppered flask; deliver out 5 ml. of water into the flask and again weigh. Deliver out successively a number of volumes, and again weigh. The following volumes may be delivered:

0 to 5 ml., 5 to 10 ml., 10 to 15 ml.

15 to 20 ml., 20 to 25 ml.

Record your results as given below and calculate the correct volumes for different ranges of the burette (a burette may have non-uniform errors in graduations):

Temperature (say 24°). Density at (say 24°)=0·9963.

	Apparent volume	First weight of the flask	Second weight of the flask	Weight of 5 ml. of water.	Correct volume W/D	Error
1.	0 to 5 ml.	25·0000g.	29·9986 g.	4·9986 g.	$\frac{4{\cdot}9986}{0{\cdot}9963}$	
2.	5 to 10 ml.					
3.	10 to 15 ml.					

Experiment 3—*Calibration of a flask*—The flask is first cleaned and thoroughly dried: it is then counterpoised on a balance, and distilled water, having a temperature of about 20°, is run into the flask until the lower edge of the meniscus stands at the level of the volume mark on the neck. Any water which may have got on the neck above the mark should be removed by means of the filter paper. The weight of the flask is again taken and from the two weighings, the weight of water in the flask is known. The volume of water corresponding to this weight is then calculated from the density of water for the given temperature.

II Molecular Weight of Volatile Liquids From Their Vapour Densities.

It is known from the Avogadro's hypothesis, that two gases at the same temperature would contain the same number of molecules in the same volume. Density of a gas or vapour may be determined with respect to hydrogen. This is known as *vapour density*. Since the molecular weight of hydrogen is 2, *the molecular weight of a gas or vapour*=2× *its vapour density*. The two well known methods of determining vapour densities are:

(*i*) Dumas' method, and (*ii*) Victor Meyer's method.

Experiment 4—*To determine the molecular weight of chloroform by Dumas' method.*

In this method, a glass bulb (B) with a long neck is dried and weighed. Sufficient liquid is introduced into the bulb by warming the bulb, dipping the neck into the liquid and cooling. The bulb is then supported in a water bath (A), or an iron pot containing water, oil, or melted paraffin wax, heated above the boiling point of the liquid of which vapour density is to be determined. Volatilisation rapidly occurs, the air being expelled through the tip of the bulb, which project above the surface of the liquid in the bath. When the rush of vapour ceases, the neck of the bulb is sealed off and the temperature of the bath read off on the thermometer. The bulb is removed from the bath, cooled, cleaned and reweighed. The tip of the neck of the bulb is scratched with a file and broken under water. The latter rushes into the bulb and fills it completely. The bulb full of water is weighed. The barometric pressure is also noted.

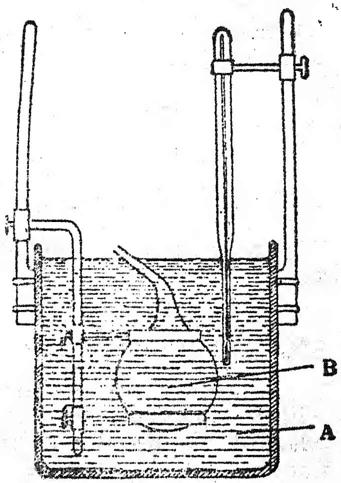

Fig. 14

The experiment may be tried with chloroform or hexane.

Weight of the Dumas' bulb $=40{\cdot}9555$ g.

Weight of the bulb filled with chloroform vapour $=41{\cdot}7318$ g.

Temperature of bath when sealed $=89°$

Weight of bulb filled with water $=309{\cdot}61$ g.

Pressure (atm.) $=752{\cdot}3$ mm.

Temperature $=30{\cdot}6°$

Calculations—

Weight of water in the bulb $=309{\cdot}61-40{\cdot}9555$ g. $=268{\cdot}6545$ g.

Therefore, the capacity of the bulb at $30{\cdot}6°$ and $752{\cdot}3$ mm. is $268{\cdot}6545$ ml.

It will be seen from tables that the relative density of air at this temperature and pressure is $0{\cdot}001143$.

Therefore, the weight of air in the bulb $=268{\cdot}6545\times0{\cdot}001143=0{\cdot}3070$ g.

Hence the weight of evacuated bulb $=40{\cdot}9555-0{\cdot}3070$ g. $=40{\cdot}6485$ g.

Therefore, weight of chloroform vapour in the bulb

$$=41{\cdot}7318-40{\cdot}6485 \text{ g.}=1{\cdot}0833 \text{ g.}$$

Weight of 1 ml. of hydrogen at 760 mm. and 0° (273°A) is 0·00009 g.

Therefore, the weight of hydrogen occupying 268·6545 ml. volume at 752·3 mm. and 89° (i.e. 362°A)

$$=\frac{752{\cdot}3\times 268{\cdot}6545\times 273\times 0{\cdot}00009}{760\times 362}\text{ g.}$$

$$=0{\cdot}01847 \text{ g.}$$

Hence the vapour density of chloroform $=\frac{1{\cdot}0833}{0{\cdot}01847}=58{\cdot}6$.

Thus the molecular weight of chloroform $=2\times 58{\cdot}6=117{\cdot}2$. Correct value is 119·5.

Experiment 5—*To determine the molecular weight of carbon tetrachloride by Victor Meyer's method.*

The apparatus consists of a long glass tube with a bulb and a side tube (fig. 15). The whole of it is placed in an outside jacket made from a metal which contains water in the lower bulbous part. This when heated provides steam and keeps the whole apparatus at a temperature which must be constant and higher than the boiling point of the substance (the temperature need not otherwise be known). The side tube delivers into a graduated tube in a trough of water. The long tube is heated in the bath until no more bubbles of air escape; then the side tube is placed under the graduated tube, the cork of the top of the long tube is taken out, and the weighed quantity of the liquid in a small stoppered bottle (known sometimes as Hoffman's bottle) dropped into the heated bulb, the cork being quickly replaced. A little asbestos fibre or a little mercury is placed at the bottom of the bulb to prevent fracture on dropping the stoppered bottle.

The liquid quickly vapourises and the *vapour* (which does not diffuse to the top of the narrow tube) *displaces its own volume of air*, which is collected in the graduated tube. When no more bubbles come off, the volume of air is read off and corrected for pressure and temperature.

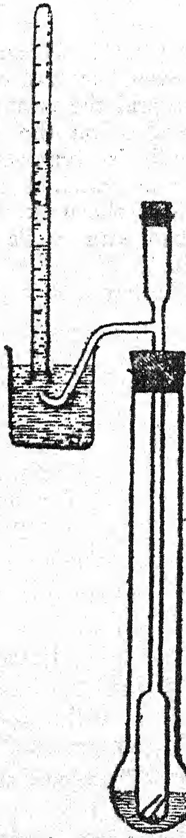

Fig. 15

For reading the volume, the graduated tube is brought to a long jar filled with water, and the level of water inside and outside is made equal.

Observations—Weight of the Hoffmann's bottle		$=0{\cdot}5760$ g.
	Weight of the bottle+liquid	$=8{\cdot}7376$ g.
	Weight of the liquid	$=0{\cdot}1616$ g.
	The volume of air displaced	$=28$ ml.
	Temperature of water	$=30°$
	Atmospheric pressure	$=752{\cdot}7$ mm.
	Vapour tension from table at 30°	$=31{\cdot}7$ mm.

Calculations—Atmospheric pressure—vapour tension

$$=752{\cdot}7-31{\cdot}7 \text{ mm.}=721 \text{ mm.}$$

Weight of hydrogen at 30° (or 303°A) and 721 mm.

$$=\frac{28\times 721\times 273\times 0{\cdot}00009}{760\times 303}=0{\cdot}002155 \text{ g.}$$

$\therefore$ the vapour density of the liquid$=0{\cdot}1616/0{\cdot}002155=75$

Therefore the molecular weight of the liquid$=2\times 75$
$=150$

III. Molecular weight determinations on the basis of Raoult's law

In 1883, Raoult made an interesting observation that a *gram molecule of all substances* (unless the substance dissociates or associates in or chemically reacts with the solvent) *dissolved in the same amount of a solvent would produce the same degrees of lowering of the freezing point of the solvent, and also produce the same degrees of elevation of the boiling point of the solvent.*

K_f=molecular lowering of freezing point.

It is defined as the lowering in the freezing point when one gram-molecule of the substance is dissolved in 100 g. of the solvent. Sometimes it is expressed in terms of 1,000 g. of the solvent also.

K_f for 100 g. of the solvent$=10\times K'_f$ for 1,000 g. of the solvent.

Thermodynamically.

K_f (for 100 g. of the solvent)$=\dfrac{0{\cdot}01987\times T^2}{L}$, where T is

the freezing point (absolute temp.) of the pure solvent, and L is the latent heat of fusion.

Solvent	Freezing point t°	Latent heat L	K_f for 100 g. of the solvent
Water	0°	79·8 cal	18·58°
Benzene	5·4°	30·4	51·20°
Acetic acid	16·6°	44·7	39·00°
Nitrobenzene	5·72°	22·5	68·7°

Similarly, K_b is the molecular elevation of the boiling point. It is defined as the elevation in boiling point of the solvent when a gram-molecule of the solute is dissolved in 100 grams of the solvent. Thermodynamically,

$$K_b = 0{\cdot}01987 \times T^2/L$$

where T is the boiling point on the absolute scale and L the latent heat of vaporisation.

Solvent	Boiling point (760 mm.)	Latent heat L	K_b for 100 g. of the Solvent
Water	100·0°	539·5 cal.	5·13°
Benzene	80·2°	94·4	25·7°
Acetone	56·2°	124·5	17·2°
Chloroform	61·2°	59·5	38·6°
Ether	34·6°	83·9	21·1°

Experiment 6—*To determine the molecular weight of sucrose by the freezing point depression method.*

Set up the Beckmann thermometer by the adjustments of the quantity of mercury in the bulb in such a manner that when

pure water freezes, the mercury in the thermometer stands at a mark near 5° on the Beckmann scale.

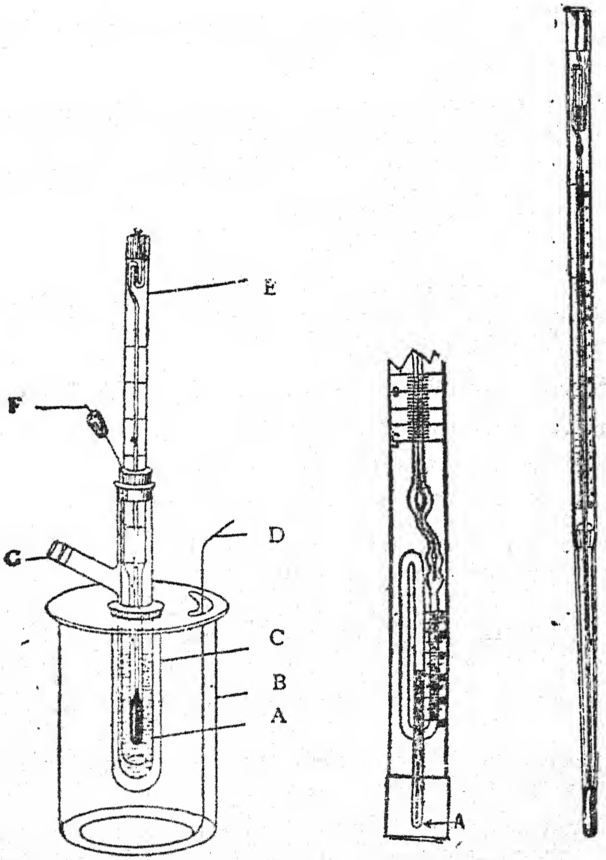

Fig. 16

The apparatus used for the determination of the freezing point is shown in the fig. 16. The weighed amount of water is taken in the inner tube A (water may be measured in ml. and then the volume may be multiplied by the density). This is enclosed in a wider tube C, which in turn is immersed in a freezing mixture in an outer jar B. The object of the air jacket between the two inner tubes is to make the cooling slow, so that the accurate readings may be made. The liquid is stirred, and the temperature at which mercury in the Beckmann thermometer becomes steady is read off. In fact, a little supercooling takes place in the

beginning, it is released by stirring and the mercury thread suddenly shoots up and becomes stationary at a temperature which is the freezing point.

A weighed amount of sucrose is then introduced through the side arm G in the inner tube, dissolved and the process of determining the freezing point repeated.

Further freezing points are taken with additional quantities of the substance introduced and dissolved in the solvent.

Calculations—The molecular weight of the substance

$$=\frac{100\times K_f\times a}{\triangle T\times b}$$

where $\triangle T$ is the depression of the freezing point caused by a g. of the solute in b g. of the solvent, and K_f is the molecular lowering of the freezing point (18·58 for water).

Observations—Solvent (water) taken=25·0 ml.=25·0 g.

Sucrose introduced=0.6204 g.

Beckmann reading with pure water=4·32°

Beckmann reading with sucrose solution=4·095°

Depression in freezing point, $\triangle T=4{\cdot}23-4.095=0{\cdot}135°$

Therefore, the molecular weight of sucrose

$$=\frac{100\times 18{\cdot}58\times 0{\cdot}6204}{25\times 0{\cdot}135}=340$$

The correct value corresponding to $C_{12}H_{22}O_{11}$ is 342.

Experiment 7—*To determine the molecular weight of sucrose by the elevation of the boiling point method.*

It is not necessary to use the Beckmann thermometer in this case; any thermometer which reads up to one-tenth of a degree would do. In case the Beckmann is used, the mercury in the bulb of the thermometer is so adjusted that it stands at the mark in the neighbourhood of zero on the scale.

The apparatus is described in the figure 17. It consists of an inner graduated wide tube B enclosed in another wider tube A provided with a projecting side tube P. The solvent is taken in the inner tube B and the volume of the solvent at any moment can be read on the graduations. Water is heated in a conical flask E and the steam from this flask is carried through the delivery tube D and bubbles through the solvent in B and escapes through a hole in the same (G). The steam as it condenses

trickles out through P. Boiling points are read off on the thermometer C. Boiling point of the pure solvent is first determined.

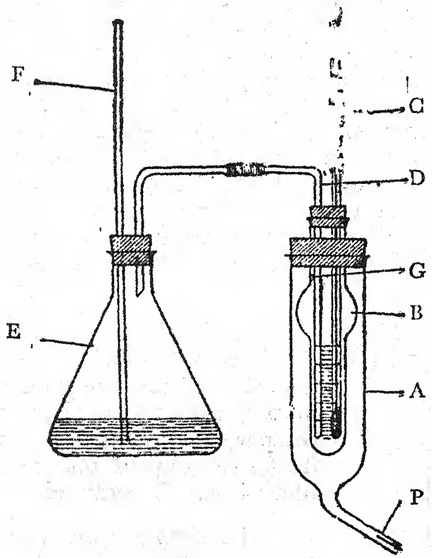

Fig. 17

A weighed amount of sugar is then introduced by quickly taking out the cork and immediately placing it back, and the boiling point of the solution is again determined while the steam is bubbling through. The volume of the solvent is also read off on the scale at the same instant.

Observations—Amount of sucrose introduced$=1{\cdot}7260$ g.

Boiling point of pure water	$=100°$
Boiling point of the sucrose solution	$=100.236°$
Elevation of the b. pt., ΔT	$=0{\cdot}236°$
Volume of the solution	$=11$ ml.
The amount of the solvent	$=11$ g. approx.

$$\text{Molecular weight}=\frac{100\times K_b\times a}{\Delta T\times b}$$

where K_b is the molecular elevation of the boiling point ($5{\cdot}2°$ for water). a is the weight of sugar dissolved in b g. of the solvent, and ΔT is the elevation of the boiling point.

$$\text{Molecular weight of sucrose}=\frac{100\times 5{\cdot}2\times 1{\cdot}7260}{11\times 0{\cdot}236}=340.$$

IV. Viscosity of Liquids.

When a liquid flows through a narrow tube, the velocity of flow will depend, in the first place, on the force which produces the flow. All parts of the liquid, however, do not move through the tube with the same velocity; the layers next to the sides of the tube move more slowly than the middle layers. There is thus a shearing, or a movement of the different layers past one another in the direction of flow; and this displacement of different layers relatively to one onother is opposed by the internal friction or *viscosity* of the liquid. The same amount of various liquids flowing through the same capillary tube does not take the same time to flow and this difference is due to their difference in viscosity.

The *coefficient of viscosity*, or simply known as *viscosity* has the dimension, $ML^{-1}T$, and is measured in C.G.S. units. The determination of the absolute viscosities is not always convenient. But it is easier to compare the viscosities of two liquids and if the viscosity of one be known, of the other is also determined.

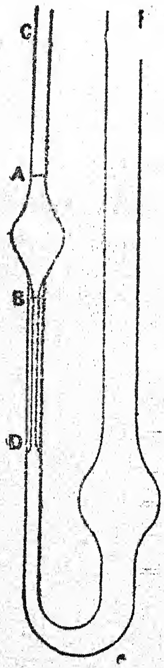

Fig. 18

The simple apparatus used for determining the relative flow is known as *Ostwald's viscometer*. It consists of a fine capillary tube, through which a definite volume of liquid, namely, that contained between the two marks A and B, is allowed to flow under the force of its own weight. In the actual experiment, a known volume of the liquid, say 10 ml., is introduced into the wider U-limb (Fig. 15). A piece of rubber tubing is attached to the narrow U-limb, and by sucking the air, the liquid is sucked up a little beyond the mark A into the narrower limb. The liquid is then allowed to flow back through the capillary and the time required for the surface of the liquid to pass from the mark A to mark B is noted by means of a stop-watch.

If the two liquids, with viscosities η_1 and η_2 have the densities d_2 and d_1 and their time of flow, when the *same volume* of the two has been introduced into the viscometer, be t_1 and t_2 then:

$$\frac{\eta_2}{\eta_1}=\frac{d_2 t_2}{d_1 t_1}.$$

The viscosities are usually determined with respect to water.

Experiment 8—*To find out the viscosity of benzene*—Clean up the viscometer with chromic acid and finally with distilled water. Arrange a small bath of constant temperature, 25°, in which the viscometer can for the most part be vertically held. Pipette out 10 ml. of distilled water and introduce it in the bulb. When water has attained the temperature of the viscometer, suck up the liquid a little beyond the mark A, and then allow it to re-flow under its own weight. Start the stop-watch when the liquid is just at A, and stop the watch immediately the liquid passes the point B. This is the time of flow for water. Repeat the experiment three or four times.

Dry up the viscometer, and introduce 10 ml. of benzene into it, and when the liquid has attained the temperature of the bath, determine its time of flow in the same way as in the case of water.

By means of specific gravity bottle, determine the relative density of benzene at the same temperature.

Viscosity of benzene

$$= \frac{(\text{time} \times \text{density) for benzene}}{(\text{time} \times \text{density for) water}} \times \text{viscosity of water.}$$

Viscosity of Liquids

Liquid		Viscosity at					
		0°	10°	20°	25°	30°	40°
Water	..	0·0179	0·0131	0·0101	0.0089	0.00803	0·00660
Mercury	..	0·0169	0·0162	0·0155	...	...	...
Ethyl alcohol	..	0·0177	0·00145	0·0119	..	0·00989	0·00827
Ether	..	0·00286	0·00258	0·00234	..	0·00212	–
Benzene	..	0·00902	0·00759	0·00649	..	0·00562	0·00492
Chloroform	..	0·00700	0·00626	0·00564	..	0·00511	0·00455

Relative viscosity of normal solutions with respect to water.

NH_4OH	25°	1·02	NH_4Cl	17.6°	0·98	KCl	17·6°	0·98
HCl	25°	1·07	NaOH	25°	1·24	KI	17·6°	0·91

V. Surface Tension of Liquids.

The surface of all liquids behaves like a stretched skin, and there exists a pull in the surface of all the liquids, in some less

and in some more. This pull is known as tension of the surface. *Surface tension* is the force per unit length of a line drawn on the surface and acts at right angles to the line, tending to pull the surface apart along the line. The dimensions of the surface tension (force/length) are MT^{-2}. It is expressed in dynes per centimeter.

The formation of drops depends upon the surface tension of the liquid. All liquids would not give the same number of drops from the same volume of liquid, if allowed to fall from the same surface. If the densities of the two liquids be d_1 and d_2 and their surface tensions be γ_1 and γ_2, the number of drops n_1 and n_2, *dropping* from the same dropping tube and employing the same volume of the two liquids is represented by the following equation:—

$$\frac{\gamma_1}{\gamma_2}=\frac{n_2 d_1}{n_1 d_2}.$$

The apparatus used for the determination of surface tension by the drop method is known as *stalagmometer* (Traube's). It consists of a dropping tube with a capillary, the end of which is flattened out in order to give a larger dropping surface, and the surface is then carefully ground flat and polished (Fig. 19. The capillary is sealed on to a tube of wider bore on which a bulb is blown, and on the stem of the tube two marks are etched, one above and one below the bulb.

Care must be taken to ensure that the dropping surface is perfectly free from greasiness.

Experiment 9—*To determine the surface tension of benzene.* Clean stalagmometer with chromic acid, and finally with water, and suck in distilled water beyond the upper mark. Allow water to drop, and begin counting the number of drops when the water level reaches the upper mark on the stem. The counting is finished when the liquid reaches lower mark. An accuracy up to half-a-drop is sufficient. The rate of dropping in these experiments should not be more then 20 drops a minute. This gives the '*drop number*' *of water.*

Dry out stalagmometer, and determine the drop numbers for benzene in exactly the same way. Determine the densities and calculate the surface tension of benzene by the formula given above.

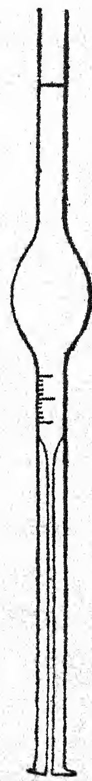

Fig. 19

Liquid	Temperature	Surface tension Dyne/cm.
Water	20°	72·6
	30°	71·1
Ethyl alcohol	20°	22·03
	40°	20·2
Ether	20°	16·5
Benzene	20°	29·2

Expression for the drop weight method—The equation given above for the surface tension can easily be derived from theoretical considerations: A drop just held at a surface or just dropped from the surface balances two forces: (*i*) the gravity force exerted on the drop given by $v.d.g$ where v is the volume of the drop, d its density and g gravity, and (ii) the force tending to uphold the drop, given by $2\pi r\gamma$, where $2\pi r$ is the circumference of the circular surface of radius r and γ is the surface tension (the force per unit length). The two forces are balanced when

$$2\pi r\gamma = v.d.g.$$

It is, however, more convenient to measure the number of drops in a volume V for the two liquids than to find the weight of each drop. If the number of drops be n in a volume V of the liquid of density, d, the weight of each drop is Vd/n.

While comparing the two liquids of densities d_1 and d_2 having the same volume V, and the number of drops n_1 and n_2, in the same volumes, we get:

$$2\pi r\gamma_1 = Vd_1g/n_1$$

and

$$2\pi r\gamma_2 = Vd_2g/n_2.$$

From this

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2d_1}{n_1d_2}$$

VI. Refractive Index

When a ray of monochromatic light passes from one transparent medium into another of different optical density, it is refracted except when it enters perpendicularly to the surface of contact between the two media. The angle between the ray in the first medium and a perpendicular to the dividing surface is known as the *angle of incidence*, i, and the corresponding angle in the second medium the angle of *refraction*, r. The sin i and sin r

are directly proportional to the velocities of light in the two media, The ratio sin $i/\sin r$ is termed the *index of refraction or refractive index, i.e.*

$$\mu=\frac{\sin i}{\sin r}=\frac{v_1}{v_2},$$

where v_1 and v_2 are the velocities of light in the two media. Since the ratios of these velocities in air and in water is 4/3, the index of refraction of water with respect to air is refraction of water with respect to air is also 4/3, *i.e.*, 1·333.

When the incident angle is increased, the angle of refraction r is also increased, and attains its maximum value when the ray of incidence enters horizontally at 90° (known as *grazing incidence*). Since sin 90°=1, sin $r_c=1/\mu$. At this angle r_c, the ray passing from the denser medium to the lighter would emerge parallel to the dividing surface; if the angle is greater than r_c, total reflection would take place. The angle r_c is known as the critecal angle, at which the ray emerging out of the denser medium to the lighter is parallel to the dividing surface. The critical ray furnishes the basis of observation of the refractive end point used in many refractometers.

Abbe's refractometer—It is largely used for determining refractive indices since it is simple, easy to manipulate and since it needs

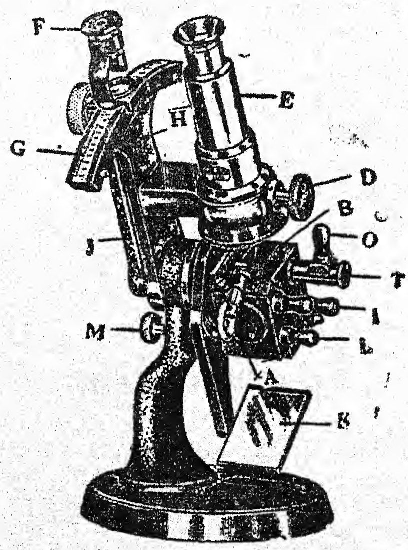

Fig. 20

only a small amount of the liquid for experiment. For measuring refractive indices with this instrument, only a few drops, sufficient to form a film, are placed between the prisms of the instrument.

The refractometer consists of four essential parts: (*i*) a telescope *E* provided with an objective, an eye-piece and a cross-hair disc. The purpose of the telescope is to form an image of the border line of total reflection at the intersection of the cross-hairs where the image may be observed. (*ii*) Two similar glass prisms (Abbe prisms) of high refractive index cemented into hollow, water jacketed, mounting cases so constructed that when temperature control is required, water may be circulated about the prisms. The exposed surfaces of the upper prism *B* are highly polished, while the hypotenuse surfaces of the lower prism *A* which serves solely for the purpose of illumination, is finely ground. The lower prism mount is hinged to the upper prism mount and the latter is rigidly attached to the index arm or alidade. When the two prisms are clamped together, a space of about 0·1—0·15 mm. separates their surfaces. (*iii*) The sector *H* is a metal arm to which the telescope is rigidly attached. One end of the sector is attached to the upright of the base in such a manner that the whole sector can be rotated about an axis, which coincides with the axis of rotation of the Abbe prism so that various conditions of illumination can be accommodated. On the upper end of the sector, a scale *G* is mounted which is graduated directly in terms of refractive index of the *D* line (sodium light) at 20°*C*. An alidade or movable arm *J* rests against the sector, but it can be rotated as a unit with the Abbe prism independently of the sector. The upper end of the alidade bears an idex mark which moves along the edge of the sector scale when the arm is rotated. Sometimes a magnifier *F* is attached to the alidade to facilitate the reading of the index scale. A screw *M* is used to make fine adjustment of the border line at the cross-hairs.

(*iv*) Compensating prisms are used to correct for the dispersion of light. Thus when white light is used in the place of sodium light the beam is split up into coloured beams, since short wave lengths of light are refracted to a greater extent than are long wave lengths. Unless this dispersion is compensated for in some way, the border becomes a broad,vari-coloured band which cannot be brought into accurate coincidence with the cross-hairs of the telescope. The compensator functions to bring the various wave lengths of light together again. It is placed between the upper prism and the eyepiece and is rotated by means of the milled head *D*.

Experiment 10—*To determine the refractive index of a given liquid.*

Test the correctness of the Abbe's refractometer readings by a test plate, the refractive index of which is known and is etched on the plate. In the absence of a test plate, a liquid of known refractve index may be taken and the instrument standardised with it.

Clean the upper prism of the refractometer with cotton saturated with alcohol, clamp the prisms together loosely, introduce 2 or 3 drops of the given liquid into the groove at the side of the prisms and clamp the prisms together firmly. Adjust the mirror K so that the light is reflected upon the lower prism, and rotate the alidade until the border line between the light and the dark halves of the field of view exactly coincides with the cross-hairs of the telescope rotating the compensator prisms to obtain a sharp uncoloured border line if necessary. Read the refractive index of the liquid directly from the graduated sector scale to the fourth decimal place. Move the alidade and again determine the refractive index until three readings are obtained. Take the mean of these readings.

The refractive index is expressed as $N_D^{25}=1{\cdot}4733$, indicating that the refractive index has been determined at temperature 25° for the D line (sodium light).

VII. Polarimeter and Specific Rotation

The instruments used to measure the optical activity of liquid substances are called polariscopes or polarimeters and saccharimeters. Polarimeters permit the angle of rotation to be read off in degrees or fractions of a degree on a circle, while saccharimeters are usually constructed and set to give readings directly in terms of percentage of sugar. Usually *hair-shadow* instruments known at Duboscq, Laurent and the Schmidt and Hansch polarimeters are used for experimental work.

The optical parts of the polarimeter are shown in the figure 21. Monochromatic light (usually sodium) from the source L

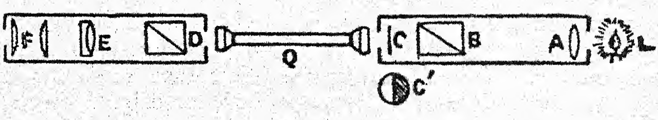

Fig 21

passes though the lens A, which renders the rays of light parallel, and then passes through the polarizing prism B, which renders the light ray plane-polarized. It then passes through

the observation tube O, which contains the substance being examined and thence through the analyzer prism D. The field of view is observed through the telescope FE. The circular opening of the tube carrying the polarizer is one-half covered with a thin quartz plate as illustrated

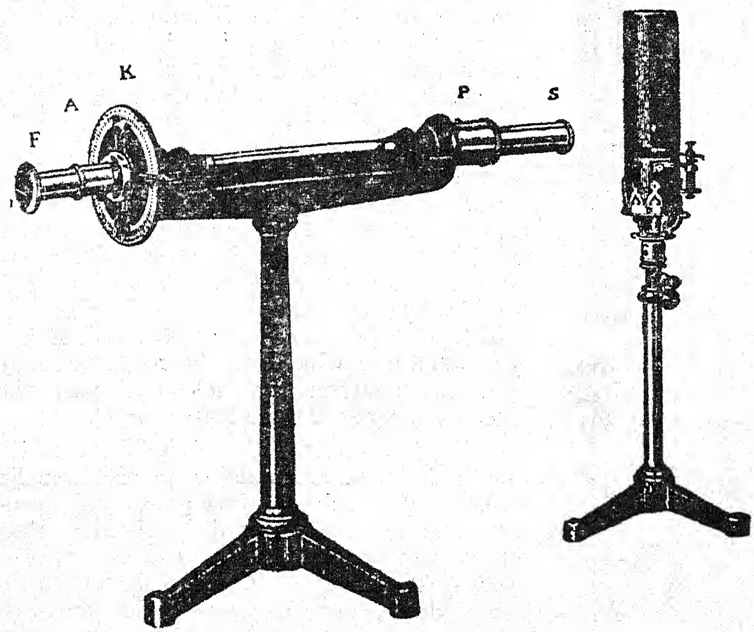

Fig. 22

in C′ the thickness of which is so adjusted that the light in passing through the plate is altered in phase by half-a-wave-length but remains plane-polarized. In this way two beams of polarized light are produced. If the polarizer is rotated so that the plane of polarization forms an angle X with the quartz plate, the planes of polarization will also be inclined at an angle 2X. This is termed the *half-shadow angle*. On rotating the analyzer, a position will be found at which one beam of light will be completely, and the other only partly, extinguished. One-half of the field of view will then appear dark while the other half will remain light. Upon rotating the analyzer further through angle 2X, a second position will be found at which the second beam of light will be extinguished while the first beam becomes visible. At this position of the analyzer that half of the field which formerly appeared dark will be light and formerly light will be dark.

When the analyzer occupies an intermediate position, a field of view of uniform brightness will appear, and this is the position at which the analyzer should be set.

The complete polarimeter is shown in figure 22. At the end *S*, which is directed towards the source of illumination, is the lens. The polarizing prism is at *P*, and it is connected with a lever by means of which it can be rotated to alter the angle of half-shadow. The observation tube is placed in the central part of the instrument and protected from extraneous light by a hinged cover. The analyzer is placed at A and it can be rotated independently of the graduated circle by means of a screw. This permits the correction of the instrument. *F* is a telescope with the eyepiece by means of which the field of view is observed, *K* is a graduated disc which can be made to rotate with the analyzer and telescope past the fixed verniers on the graduated circle.

The observation tube, (Fig 23) in which the liquid to be examined is placed, usually consists of a tube of thick glass with accurate ground ends, closed by circular glass plates with parallel sides which are pressed against the ends of the tube by means of screw caps. Other polarimeter tubes are constructed with a jacket through which water may be circulated to give constant temperature. Since the unit of length in polarimetric measurements is 1 dcm., the observation tubes are usually of 1 dcm. length, or some multiple or some fraction of it.

Fig. 23

Experiment 11—*To determine the specific rotation of sucrose.*

Adjust and determine the zero point of the polarimeter. Set up the polarimeter so that the polarizer end is in direct line with the bright sodium flame and about 4 to 6 inches from it. Place 10 cm. observation tube filled with distilled water in the tube-holder between the polarizer and the analyzer and focus the telescope eyepiece in the line bisecting the field of view, rotating the analyzer if necessary in order to obtain unequal illumination of the two halves of the field. Now determine the zero point by rotating the analyzer until equal illumination of the two halves of the field is obtained. The position should be approached several times from either side of the

zero point and the mean taken. Since the zero point is altered by alteration of the angle of half-shadow, the lever which rotates the polarizer must be set before the zero point is determined.

Prepare a 25 per cent. solution of sugar (25 g. accurately weighed and raised to 100 ml. in a graduated flask). Rinse the observation tube with this solution and then fill it up with the sucrose solution. Determine the value of the angle of rotation.

From this angle of rotation and from the strength of the sucrose solution, calculate the specific rotation.

The specific rotation is defined as the angle of rotation in degrees through which the plane of polarization of monochromatic (D) light is rotated by passage through a liquid containing 1 gram of the active substance in a volume of 1 ml. determined in a tube having a length of 1 decimeter.

The specific rotatory power is calculated by the following expressions :

For liquids : $[\alpha]^{t}_{D} = \frac{a}{ld}$.

For solution : $[\alpha]^{t}_{D} = \frac{100a}{lpd} = \frac{100a}{lc}$.

a=observed rotation in degrees at the temperature t and using sodium light (D).

l=length of the tube in decimeters.

d=the specific gravity of the liquid or solution at $t°$.

p=the concentration of solution expressed as the number of grams of active substance in $100g$. of solution.

c=concentration of solution expressed as the number of grams of active substance in 100 ml. of solution.

If the substance is dextro, the plus (+) sign and if the substance is laevo, the minus(—) sign must be shown before the specific rotation.

Substance	Solution	Concentration in 100 ml.	Specific rotation $[a]^D$ at 25° for D light
Camphor, natural ...	Alcohol	10 g.	+41 to +42°
Dextrose ...	Water	10 g.	+52·5 to +53°
Lactose ...	Water	10 g,	+52·2 to +52·5°
Ephedrine sulphate...	Water	5 g.	−29·5 to −32°
Chaulmoogra oil- ...	Chloroform	10 g.	+48 to +60°

VIII. Duboscq Colorimeter

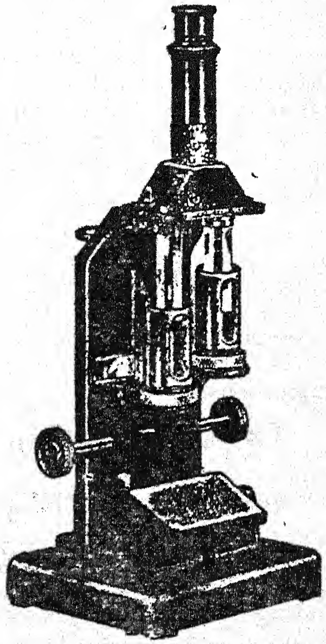
Fig. 24

The essential parts of the instrument consist of plungers, cups, a reflecting mirror, a compound prism, an observation microscope and adjustments. Two prisms of optical glass, hexagonal in form, matched for colour and with optically plane and parallel ends are attached to the frame of the instrument by threaded metal adapters. Two detachable cups in which the liquids under examination are placed are threaded on movable stages beneath the plungers. These cups are made of glass fitted into metal casings and have bottoms made of optically inactive glass discs. An adjustable mirror with two reflecting surfaces is so placed that light can be reflected through the cups. A compound prism is built above the plungers in a dust-proof housing in such a manner as to bring the light beams through each cup to a common axis, light from one cup illuminating one-half of a circular field and light from the other cup illuminating the other half. An observation microscope, by which the observer views both fields of illumination with one eye is focussed on the two fields. Adjustments are provided whereby the cups may be raised or lowered, the level of each cup being shown on a scale and vernier.

Adjust the colorimeter, place it before an ample source of light (say sunlight), and regulate the mirror so that the two halves of the field are of the same colour and equal brightness. Fill one of the cups about one-half full with the known solution and the other cup about one-half full with the unknown. Replace the cups in the instrument and raise them until the plungers come in contact with bases. Adjust the liquid depth in the cup containing the known solution to any convenient level preferably to an exact number of millimeters. Raise or lower the cup containing the unknown liquid until both the halves of the field are of the same colour and intensity. Take a few independent readings with the cups at different levels.

If C_1 and D_1 are the respective concentration and depth of the known solution, and C_2 and D_2 the corresponding for the unknown, then

$$C_1 \times D_1 = C_2 \times D_2$$

and therefore, the concentration of the unknown solution, C_2, is given by:

$$C_2 = \frac{C_1 \times D_1}{D_2}.$$

IX. Heat of Neutralisation of Acids and Bases.

On the basis of the ionic theory, the process of neutralisation of hydrochloric acid by caustic soda is represented by the equation:

$$Na^+ + OH^- + H^+ + Cl^- = Na^+ + Cl^- + H_2O.$$

Thus this process consists of merely the combination of hydrogen ions with hydroxyl ions to form undissociated water. Therefore, in the case of strong acids and strong bases at fairly low dilution, we find the heat of neutralisation to be the same for all acids and bases, *viz.*, 13·7 Calories (or 13,700 calories).

The principle on which the determination of heat of neutralisation is based is the same as applied in ordinary calorimetric experiments. A thermos flask may be used as a calorimeter; or it may consist of two beakers one fitting inside the other. The inner beaker is suspended in the outer one by means of an aluminium wire and leaves an air gap between the two. The water equivalent to the inner beaker (which, in fact, acts as a calorimeter) is determined in the usual way (by adding a known amount of hot water to a known amount of cold water, and noting down the final temperature of the mixture).

The thermometer used reads up to 0·1° and is graduated usually up to 50°. The thermometer itself can serve as a stirrer.

Experiment 12—*To measure the heat of neutralisation of hydrochloric acid by sodium hydroxide*—First, determine the water equivalent to calorimeter from the following readings:

Weight of cold water..................m_1 *g*.
Temperature of cold water.........t_1°.
Hot water added........................m_2 *g*.
Temperature of hot water............t_2°.
Final temperature of mixture.........t_3°

If water equivalent to calorimeter be W, then

$$(m_1 + W)(t_3 - t_1) = m_2 (t_2 - t_3)$$

From this equation find out the value of W.

Prepare 250 ml. of N NaOH solution and place it in the calorimeter. Also prepare 250 ml. of N HCl (if the prepared HCl is of some other strength, find out its volume corresponding to 250 ml. of N NaOH). Note down the initial temperature of NaOH and HCl solutions. It is preferred if both of them are at the same temperature, otherwise the mean of the two temperatures may be taken as the initial temperature. Add the HCl solution to the NaOH solution in the calorimeter. Mix well and quickly note the maximum temperature reached. Record the readings as follows and calculate the heat of neutralisation.

Volume of the acid.................. v_1 ml.

Volume of the alkali.............. v_2 ml.

If their specific heats be taken to be unity and densities also unity (the same as of water), their masses will correspond to v_1 and v_2 g.

Initial mean temperature of acid and alkali...... $t_1°$.
Final temperature.. $t_2°$.
Rise in the temperature.......................... $(t_2-t_1)°$
Water equivalent to calorimeter.................... W.

Hence heat produced during neutralisation

$$=(v_1+v_2+\mathrm{W})\ (t_2-t_1) \text{ calories.}$$

So much heat is produced when v_1 ml. of N HCl (equivalent to v_2 ml. of NaOH) have been neutralised. From this find out the heat produced when 1,000 ml. of N HCl would have been neutralised.

Heat of neutralisation is thus $\frac{1000}{v_1}(v_1+v_2+\mathrm{W})\ (t_2-t_1)$

Sometimes the values are expressed in terms of "large" Calories, or a kilogram calorie=1,000 calories.

X. Velocity of Chemical Reactions.

The velocity of a chemical reaction is given by the following equation:

$$dx/dt=k(a-x)\ (b-x)\ (c-x)\ldots$$

where x represents the amount in gram-molecule of the substances changed in time t, and a, b, c. . represent the initial concentration (in gram-molecules per litre) of the interacting substances.

In cases, where only one molecular species undergoes change, that is the reaction is unimolecular, the velocity simplifies to the following :—

$$\frac{dx}{dt}=k\,(a-x)$$

On integration,

$$k=\frac{1}{t}\log\frac{a}{a-x}=\frac{2\cdot303}{t}[\log_{10}a-\log_{10}(a-x)].$$

Experiment 13—*To determine the velocity constant of inversion of cane sugar by $N/2$ hydrochloric acid.*

Dissolve 20 grams of sugar in water and raise to 100 ml. in a standard flask. Add to 50 ml. of this solution 50 ml. of N HCl. Mix the two quickly and note the time and also the temperature (place the reaction flask in a bath maintained at a constant temperature, say 25°).

Just at the start of the reaction, withdraw 10 ml. of the reaction mixture. Boil this solution for 5 minutes, cool and then add about 10 ml. of N NaOH and raise the volume to 100 ml. in a flask. Fill up the sugar solution in a burette. Take 10 ml. of the Fehling's solution, boil it in a beaker, and, while hot, titrate it against the sugar solution taken in a burette. (At the end point, the blue colour of the Fehling's solution just discharges.) This corresponds to the totally inverted sugar in 10 ml. of the reaction mixture.

Withdraw 10 ml. more of the reacting solution and 16 ml. of N NaOH and raise to 100 ml. in a flask. Again titrate with the solution 10 ml. of the same Fehling's solution in exactly the same way and under similar conditions of boiling etc.

Again withdraw 10 ml. of the reacting solution at the intervals of 60, 90, 120 minutes. Proceed with the titration in the same way.

1 ml. of Fehling's solution=0·00475 g. of cane sugar.

Total sugar taken=a g.

Tabulate the results as follows:—

Time in minutes	Quantity of inverted sugar-z	Sugar not inverted $a-x$	log $a/(a-x)$	$K=\frac{2\cdot3}{t}\log\frac{a}{a-x}$

Note—The chemical reaction during inversion is one of hydrolysis:

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}}+H_2O=\underset{\text{glucose}}{C_6H_{12}O_6}+\underset{\text{fructose.}}{C_6H_{12}O_6}$$

The cane sugar solution is dextro-rotatory, the invert sugar (*i.e.*, the mixture of glucose and fructose obtained after hydrolysis) is laevo-rotatory, because fructose is more laevo than glucose is dextro. This change in the direction of rotation has given the term 'inversion.' The reaction can be best studied with a polarimeter.

Experiment 14—*To determine the velocity constant of the hydrolysis of methyl acetate at* 25° *in presence of* 0·5 *N hydrochloric acid.*

Prepare a standard solution of alkali, NaOH or baryta (about *N*/20,) (standardise it against a solution *N*/20 oxalic acid, using phenolphthalein as indicator). Also prepare a 0·5*N* hydrochloric acid (this can be standardised against the standard alkali solution). Take 100 ml. of 0·5 *N* HCl in a conical flask and allow it to attain a constant temperature in a thermostat or bath maintained at 25°. Also place in the same bath a small bottle containing methyl acetate.

When the liquids have attained the temperature of the bath, pipette out 5 ml. of methyl acetate, and introduce it into the conical flask containing 100 ml. of 0.5 *N* HCl. Shake the contents well and immediately withdraw 5 ml. the solution, and introduce it in 25 ml. of ice cold water in order to arrest the reaction; start the stop watch. Now quickly titrate out the acid with the standard *N*/20 alkali solution. This is the zero reading (a_0) of the reaction.

After 10 minutes, again withdraw 5 ml. of the reaction mixture, and introduce it in ice cold water as before and titrate out the acid. Take similar readings at other intervals of time, say 20, 30 40, 60, 120 minutes.

For the final reading, keep the reaction mixture standing for 48 hours (or heat the mixture to boiling for 5 minutes) and titrate 5 ml. of it against the alkali. This final reading is a_∞.

The concentration of methyl acetate$=a=a_\infty-a_0$ (in terms of the final titre value).

The initial concentration of methyl acetate is proportional to $(a_\infty-a_0)$, where a_∞ is the final titration (HCl+acetic acid) and a_0 is the initial titratian (HCl alone). The concentration of methyl acetate at time t is $(a_\infty-a_t)$ where a_t is the titre reading at the time *t*.

Time (mins.)	Titration value	Quantity hydrolysed x	Quantity unhydro-lysed $a-x$	$\log a/a-x$	$k=\frac{2\cdot 3}{t}\cdot\log\frac{a}{a-x}$
1	a_0	..	$a-a_0$		
10	a_1	a_1-a_0	$a_\infty-a$		
20	a_2	a_2-a_0	$a_\infty-a_2$		
30	a_3	a_3-a_0	$a_\infty-a_3$		
60	..	..	..		
120	..	..	..		
∞	a_∞	$a_\infty-a_0=a$	0		

Plot a graph of the concentration of methyl acetate $(a-x)$ against time, and also of logarithm of the concentration of methyl acetate against time. Calculate also the value of k (time in minutes).

XI. Preparation of Colloids

(*i*) *Ferric hydroxide sol.*—To a half-saturated freshly prepared solution of ferric chloride, add slowly, drop by drop, and with continuous stirring, an approximately $2N$ ammonium carbonate. Solution till the precipitate formed just ceases to be dissolved. Filter the solution, and dialyse in a bag of parchment paper, till free from chloride ions.

Alternate method—Add gradually to 200 ml, of boiling water 25 ml. of 1—2 per cent solution of ferric chloride. Reddish-brown sol. is at once obtained. Dialyse it as before.

For dialysis—Take a square piece of parchment paper, 12″ size; wash it with distilled water. The dried parchment gives cracks on folding, and therefore, soaking it with water is essential. Fold it round some flask and shape it into a bag, and tie it up with a thread. Place the sol in the bag, and suspend the bag with contents in a dish containing distilled water. The levels inside the bag and of water in the dish are kept the same. Change water of the dish twice a day in the beginning, and then once every day till the sol is free from unnecessary ions.

(*ii*) *Arsenious sulphide solution*—Boil about 1 g. of arsenious oxide with half-a-litre of distilled water until sufficiently dissolved. Cool the solution and filter. Pass through it a current of hydrogen sulphide (which has been washed by bubbling it through water) until it is saturated with the gas.

Remove the excess of hydrogen sulphide by bubbling through the sol a slow current of hydrogen gas. Filter the sol and dialyse if further purification be necessary.

(*iii*) *Manganese dioxide sol*—Take 500 ml. of $N/60$ $KMnO_4$ solution in a beaker. Prepare a solution of the equivalent strength of manganous sulphate (dissolve 0·428 g. of anhydrous manganous sulphate in 500 ml. of water) in another beaker. Add 6 ml. of 5% solution of gelatin to each of the two solutions. Pour into large flask both the solutions simultaneously in thin streams. A reddish-brown sol is obtained, which is dialysed.

Alternate method—To 500 ml. of $N/60$ $KMnO_4$ solution, add a dilute solution of hydrogen peroxide. The reduction is immediate and a reddish-brown sol is obtained, which is purified by dialysis till free from alkali.

(*iv*) *Antimony sulphide sol.*—Prepare a 0·5% solution of potassium antimony tartrate and fill it up in a burette. In a large beaker, take a saturated solution of hydrogen sulphide, and also keep a current of the gas bubbling. From the burette, drop slowly the solution of potassium antimony tartrate. An orange-red sol is obtained. Free it from hydrogen sulphide by passing a current of hydrogen as in the case of arsenious sulphide.

(*v*) *Colloidal sulphur*—Take 80 ml. of $3N$ sodium thiosulphate solution, interact it with 10 ml. of concentrated sulphuric acid. The colloidal sulphur is obtained. It is precipitated from the solution by addition of sodium chloride and centrifuging. But the precipitate redissolves on addition of water.

Alternate method—Dissolve rhombic sulphur in alcohol (it is slightly soluble) and pour it in a large amount of water. A milky solution of sulphur is obtained. Plastic sulphur may be similarly dissolved in alcohol and poured in water to give the sulphur sol.

Experiment 15—*Determine the precipitation values of NaCl, $BaCl_2$ and $AlCl_3$ for arsenious sulphide sol.* Prepare the solution as described above. Prepare 0·2 M solution of NaCl (11· 7 g. per litre), 0·001M $BaCl_2 . 2H_2O$ (0·2443 g. per litre) and 0·001 M $AlCl_3$ (0·1336 g. per litre).

First determine the coagulating concentrations with NaCl and then with other electrolytes. An approximate value of the coagulating concentration may be obtained by running solu-

tions of the electrolytes from a burette into a given volume, say 5 ml. of the solution.

Arrange two rows of test tubes, dry and clean, one behind the other in the test-tube stand. In the front row, take 5 ml. of the solution in each test-tube. In the back row, take 1, 2, 3, 4 and 5 ml. of NaCl solution; add to these solutions 4, 3, 2, 1 and 0 ml. of water respectively, thus bringing the total volume in each case to 5 ml. Now mix each of the test-tube contents with the corrresponding arsenious sulphide sol, and allow the sols to stand for 30 minutes. Ascertain in which case the coagulation has occurred after this period. Say, the value lies between 3 and 4 ml.

Arrange again another set similarly, and narrow down the limit of accuracy to 0·1 ml.

Proceed similarly with other electrolytes. Allow the same time for coagulation.

If the strength of the electrolyte be $x\ M$ and if the quantity required to coagulate a given solution in a particular time be v ml. when the total volume kept constant is 10 ml., the coagulating concentration is

$$\frac{x.\ v.\ 1000}{10} \text{ millimoles per litre.}$$

The reciprocals of these values represent the coagulating powers of the ions concerned, *i. e.*, Na^+, Ba^{++}, and Al^{+++}.

XII. Adsorption

When two phases, separated by a boundary, are brought into contact, there is usually a tendency of the change in concentration (usually an increase) in the neighbourhood. This fact is more marked when one of the phases is solid. This process of alteration of concentration is known as *adsorption.*

When charcoal is shaken with a solution of oxalic or acetic acid, it is found that the amount of the acid adsorbed at a given temperature is given by the equation:

$$\frac{x}{m} = a.C^{1/n}$$

Where x/m is the amount adsorbed per unit weight of charcoal (x is the amount of acid adsorbed by m g. of charcoal), C is the equilibrium concentration, and a and n *are* the constants. This equation is known as *Freundlich's isotherm.*

Experiment 15—*To verify the Freundlch's isotherm for charcoal adsorption of H^+ ions.*—Prepare $N/10$ acetic or oxalic acid solution and take into 5 numbered conical flasks (*i*) 50 ml. acid, (*ii*) 40 ml. acid, 10 ml. distilled water, (*iii*) 30 ml. acid, 20 ml. water, (*iv*) 20 ml. acid, 30 ml. water and (*v*) 10 ml. acid, 40 ml. water. Mix the solutions well.

To each of the flasks, add 2 g. of powdered charcoal and shake up the flask. Allow them to stand for 30 minutes. Shake up the contents from time to time. Filter the solutions through small filter papers, and titrate the filtrates with $N/20$ NaOH (for each titration, take 10 ml. of the filtrate). The initial acid concentration may also be represented in terms of $N/20$ NaOH values. Tabulate the results as given below and draw a graph of x/m against C. Find out the values of the constants a and n from the graph.

Temperature=

Flask No.	Contents		Initial-concen. C′	Final concen. C ′	Amount adsorbed $x=C'-C'$	Mass of charcoal m	$1/m$
	ml. water	ml. acid					
1.	50	0					
2.	40	10					
3.	30	20					
4.	20	30					
5.	10	40					

XIII. Partition Coefficient

When a substance is shaken with two solvents not miscible with each other, it gets distributed between them in a definite manner. In case the solute has the same molecular weight in each of the solvents, the distribution depends on the solubility of the substance in each of the solvents separately. If the solute be molecularly dispersed in both the solvents, and its concentrations be C_1 and C_2 in the two solvents, then for a given temperature,

$$C_1/C_2=\text{constant.}$$

This ratio is known as the *distribution* or the *partition coefficient.*

Experiment 16—*To determine the coefficient of distribution of iodine between carbon tetrachloride and water*—Prepare a saturated solution of iodine in carbon tetrachloride at the ordinary temperature. Take three glass-stoppered bottles. In them, have 30, 40 and 50 ml. of this iodine solution, and add respectively 20, 10 and 0 ml. of carbon tetrachloride (to make the total volume 50 ml.), and now add to each bottle 50 ml. of water. Shake the bottles vigorously for about an hour. Place in a bath maintained at a constant temperature. When the equilibrium has been attained, and the layers completely separated, pipette out a given volume (5 or 10 ml.) of the solution once from the non-aqueous layer and then once from the aqueous layer, and determine the concentration of iodine in each of these solutions by titrating them against a standard $N/20$ or $N/100$ hypo solution. A small quantity of potassium iodide is added to the carbon tetrachloride solution in order to ensure complete extraction of iodine.

$$\text{Partition coefficient} = \frac{\text{Conc. of iodine in 10 ml. of carbon tetrachloride layer}}{\text{Conc. of iodine in 10 ml. of aqueous layer.}}$$

Experiment. 17—*Determine the partition co-efficient of succinic acid between ether and water.* Prepare a strong solution of succinic acid in water. Take 30, 40 and 50 ml. of this solution in three glass stoppered bottles, and add 20, 10 and 0 ml. of water respectively to make the total volume 50 ml. Now add 50 ml. of ether to each of the bottles, and shake them vigorously and place them in a bath maintained at constant temperature. When the complete separation of the two layers has been affected, pipette out 10 ml. of each of the two layers and titrate the acid against a standard solution of caustic soda (or preferably baryta) using phenolphthalein as an indicator. Find out the ratio C_1/C_2 where C_1 is the concentration of succinic acid in ether layer and C_2 in water.

Partition Coefficient

C_1 is concentration in non-aqueous layer and C_2 in aqueous layer.

Iodine between CCl_4 and water (18°). (Iodine conc. in g./litre)			Iodine between CS_2 and water (18°). (Iodine conc. in g./litre).		
C_1	C_2	C_1/C_2	C_1	C_2	C_1/C_2
5·1	0·060	85	76	0·017	440
15·2	0·178	85	66	0·16	410
25·4	0·290	88	174	0·41	421

Succinic acid between ether and water (18°). (Acid conc. in g./litre)			Benzoic acid between benzene and water (20°). (Acid conc. in g./litre)		
C_1	C_2	C_1/C_2	C_1	C_2	C_1/C_2
1·3	7·0	0·912	24·9	1·50	32·8
4·1	23·6	0·175	41·2	1·95	32·9
6·1	36·5	0·167	97·0	2·19	34·1

Note—Since benzoic acid exists for the most part as associated molecules $(C_6H_5COOH)_2$ in the benzene solution, the ratio $\sqrt{C_1}/C_2$ is constant, and not the ratio C_1/C_2.

APPENDIX

Simple Inorganic Preparations

Cuprous Chloride, Cu_2Cl_2

Process—Treat 10 g. of crystallised copper sulphate, $CuSO_4, 5H_2O$, and 5 g. of NaCl (or 7 g. of cupric chloride alone) in a small flask with 3 g. of conc. hydrochloric acid and 4 g. of copper turnings. Heat over a water bath for about an hour. The green colour should have disappeared by this time. Pour the clean solution into 200 ml. of water containing a little sulphurous acid (SO_2 in water): Cuprous chloride will be thrown down as a white precipitate. Wash the precipitate by decantation with water containing a little sulphurous acid. Finally wash with alcohol and ether. Dry it in an air oven.

Reaction—

$$CuSO_4 + 2HCl + Cu = H_2SO_4 + Cu_2Cl_2\downarrow$$

Yield—4 g.

Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$.

Process—Add 4 g. of finely powdered roll sulphur (not flowers) to a solution of 32 g. of crystallised sodium sulphite, $Na_2SO_3, 7H_2O$, in 60 ml. of water, and boil the mixture in a flask for about 2 hours. By this time, all sulphur should have gone into the solution. Evaporate the solution till the point of crystallisation.

Reaction—

$$Na_2SO_3 + S = Na_2S_2O_3$$

Yield—24 g. (quantitative).

Chrome Alum

$K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$

Process—Take 10 g. of potassium dichromate in a dish and cover with 40 ml. of water. Add 8 ml. of conc. sulphuric acid, stir till all the dichromate is dissolved (enough heat is evolved by dissolving the salt). If necessary, heat for a few minutes to a clear solution. Cool the solution to 40°. Drop by drop, add ethyl alcohol to the solution with constant stirring.

The temperature would rise and hence cool in cold water bath, preferably ice. About 6·5 ml. of alcohol should thus be added (temperature should not be allowd to go beyond 50°; if necessary, drop a piece of ice in the mixture). Cool now the solution in an ice bath. Allow the contents to stand over night. Collect the crystals so formed. Recrystallise them from hot water and re-cooling (for good crystallisation add 10-12 nuclei of small crystals). Dry the crystals between the folds of a filter paper.

Reaction—

$$K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O$$

$$C_2H_5OH+O=CH_3CHO+H_2O$$

$$K_2SO_4+Cr_2(SO_4)_3+24H_2O=K_2SO_4\,.\,Cr_2(SO_4)_3\,.\,24H_2O$$

Ferrous Sulphate from Kipps apparatus

$FeSO_4.7H_2O$

Take 25 ml. of the Kipps apparatus solution (obtained by reacting FeS_2 with dil. H_2SO_4). Add some more of iron powder to the solution, till most of the sulphuric acid is consumed. Now allow the liquor to dry up (concentrate if necessary by heating gently) ; and collect the crop of crystals. Dry them in the folds of a filter paper.

Ferrous Ammonium Sulphate

$FeSO_4, (NH_4)_2SO_4.\ 6H_2O$

Procedure—Dissolve 0·1 mol. of $FeSO_4$, $7H_2O$ (ferrous sulphate crystals, mol. wt. 278), and 0·1 mol. of ammonium sulphate (mol. wt. 132); *i.e.* 28 g. of ferrous sulphate and 13·2 g. of ammonium sulphate in 40 ml. of hot water containing a little (2 ml.) of dilute sulphuric acid. Cool slowly. When the solution is cold, the crystals would gradually appear. Separate the crystals on a Buchner funnel and dry them on a filter paper.

Yield—35-39 g.

Potash Alum

$K_2SO_4.Al_2\ (SO_4)_3.\ 24H_2O$

Process from alunite—*Alunite* is K_2SO_4. $Al_2\ (SO_4)_3.\ 4Al\ (OH)_3$. The alunite or alum stone (10 g.) is calcined, *i.e.* heated dry in a dish for a long time. The calcined mass is cooled, (powdered if necessary) and treated with sulphuric acid (3 ml. conc.) and 20 ml. of water, and 5 g. of potassium sulphate extra added. The

solution is heated, and then allowed to cool down slowly. The crystals are collected and dried in the folds of a filter paper.

Reaction

$$K_2SO_4.\ Al_2\ (SO_4)_3.\ 4Al\ (OH)_3+6H_2SO_4$$
$$=K_2SO_4+3\ Al_2\ (SO_4)_3+12H_2O$$

(ii) *Process from potassium sulphate and aluminium sulphate.*—From an aluminium salt (10 g.), prepare aluminium hydroxide by adding an excess of ammonia; dissolve the aluminium hydroxide, Al $(OH)_3$, in excess of dilute sulphuric acid. Add potassium sulphate in a calculated quantity; warm, and then cool the solution, and allow the solution to crystallize. Collect the crystals and dry in the folds of a filter paper.

CHEMICAL CONSTANTS

Atomic Weights.

Aluminium	26·97	Fluorine	9·00	Oxygen	16·00
Antimony	121·76	Hydrogen	1·0078	Phosphorus	31·02
Arsenic	74·91	Iodine	126·92	Platinum	195·09
Barium	137·36	Iron	55·84	Potassium	39·096
Boron	10·82	Lead	207·21	Silicon	28·09
Bromine	79·92	Magnesium	24·32	Silver	107·88
Calcium	40·08	Manganese	54·93	Sodium	22·997
Carbon	12·01	Mercury	200·61	Sulphur	32·06
Chlorine	35·46	Molybdenum	96·0	Tin	118·70
Chromium	52·01	Nickel	58·69	Zinc	65·38
Copper	63·54	Nitrogen	14·008		

Molecular Weights and the Weights of the Radicals

Radicals	Mol. weight	Radicals	Mol. weight
Ag	.. 107.88	Cl	.. 35.46
AgBr	.. 187.80	ClO_3'	.. 83.46
AgCl	.. 143.34	ClO_4'	.. 99.46
AgI	.. 234.80	CN′	.. 26.02
$AgNO_3$	.. 169.89	Cr	.. 52.01
Al	.. 26.97	$K_2Cr_2O_7$	.. 294.21
Al_2O_3	.. 101.94	Cr_2O_3	.. 152.02
$K_2SO_4.\ Al_2(SO_4)_3\ 24H_2O$	.. 948.75	$PbCrO_4$	.. 323.2
As_2O_3	.. 197.82	Cu	.. 63.57
$Mg_2As_2O_7$	.. 310.46	CuO	.. 79.57
B_2O_3	.. 69.64	Cu_2O	.. 143.14
$Na_2B_4O_7.\ 10H_2O$	.. 381.43	$CuSO_4.\ 5H_2O$	.. 249.71
Ba	.. 137.36	$CuSO_4$	.. 159.68
$BaCl_2.\ 2H_2O$	.. 244.36	CaF_2	.. 78.08
$BaSO_4$	.. 233.42	Fe	.. 55.84
Br	.. 79.92	Fe_2O_3	.. 159.68
NaBr	.. 102.91	$FeSO_4.\ 7H_2O$	.. 278.01
CO_2	.. 44.0	$FeSO_4.\ (NH_4)_2$— $SO_4.\ 6H_2O$	.. 392.13
CO_3''	.. 60.01	FeO	.. 71.84
C_2O_4''	.. 88.02	H	.. 1.008
CaC_2O_4	.. 128.18	H_2O	.. 18.016
$H_2C_2O_4.\ 2H_2O$	.. 126.07	H_2O_2	.. 34.016
Ca	.. 40.2	HCl	.. 36.46
CaO	.. 56.08	HNO_3	.. 63.02
$CaCO_3$	.. 100.09	H_2S	.. 34.08
CaC_2O_4	.. 128.1	H_2SO_4	.. 98.08
$CaSO_4$	.. 136.14	I	.. 126.92

Radicals	Mol. weight	Radicals	Mol. weight
K	39.1	$Na_2S_2O_3$	158.1
KCl	74.55	$Na_2S_2O_3 . 5H_2O$	248.2
$KClO_4$	138.55	Ni	58.69
K_2SO_4	174.25	NiO	74.69
K_2PtCl_6	486.17	P	31.02
$K_2Cr_2O_7$	294.21	P_2O_5	142.04
KCN	65.11	KH_2PO_4	136.13
KI	166.02	$Mg_2P_2O_7$	222.61
KIO_3	214.02	$(NH_4)_3PO_4 . 12MoO_3$	1877.1
$KMnO_4$	158.03	Pb	207.2
Mg	24.32	PbO_2	239.2
MgO	40.32	$PbCrO_4$	323.2
$Mg_2P_2O_7$	222.68	$PbSO_4$	303.27
MnO_2	86.93	S	32.06
$KMnO_4$	158.03	SO_2	64.06
N	14.008	SO_3	80.06
NH_3	17.03	SO_4	96.06
NH_4	18.04	S_2O_3	112.12
NH_4Cl	53.50	SiO_2	60.06
NO_2	46.01	SnO_2	150.7
NO_3	62.01	$SrSO_4$	183.69
Na	23.00	Zn	65.38
NaOH	40.00	ZnO	81.38
Na_2CO_3	106.00	$ZnSO_4$	161.44
$NaHCO_3$	84.00	$ZnSO_4 . 7H_2O$	287.55
NaCl	58.45	$Zn_2P_2O_7$	304.80
$NaNO_2$	69·00		

SOLUBILITY TABLE

Numbers refer to grams of salt dissolved in 100 ml. in cold water. Abbreviations: *a* soluble in acids, *d* decomposed by water: *i* insoluble in water, *s* soluble in water, *v. s.* very soluble in water, *sl. s.* slightly soluble in water, *v. sl.* very slightly soluble in water.

	Acet.	Br	CO_3	Cl	CrO_4	F	I	NO_3	C_2O_4	PO_4	SO_4	S
No	119	121	7.1	35.7	50	4	159	73	3.7	v. s.	s	s
K	253	53	112	34.6	63	62	128	32	33	s.	6.8	s
NH_4	148	60	110	30	40.5	v. s.	154	118	2.5	v. s.	71	v. s.
Mg	36	91	0.01	53	212	0.009	100	200	0.07	0.02	126	
Ca	37	125	0.0015	60	16	0.0016	182	102	0.0007	0.002	0.24	0.012
Sr	s	85	0.0011	44	0.12	0.012	165	40	0.005	i.a.	0.011	
Ba	76.4	157	0.002	31	0.003	0.17	200	8.7	0.007	i.a.	0.002	d.
Al	s	v. s.	...	70	...	s	s. d.	64	i. a.	i	31	d.
Cr	s	200	...	i(233)	...	s	...	s	a	a	i. s.	d.
Zn	30	471	a	432	a	s	430	325	0.008	a	86	a
Mn	s	300	0.006	151	a	i. d.	a	d.	a	a	52	a
Ni	1.66	113	0.009	64	a	0.02	224	240	a	a	29	0.0003
Co	s	65	a	45	a	s	159	134	a	a	36	0.0003
Fe (ous)	s	109	0.0067	65	...	...	s	70	0.02	a	16	
Fe (ic)	d. i.	s.	...	75	...	...	...	s.	...	a	sl. s.	i
Ag	1.0	8.4×10^{-5}	s. s.	0.0001	0.0014	182	3×10^{-5}	122	0.0034	0.0006	0.57	i
Pb	45.6	0.46	0.0001	0.67	a	0.06	0.04	38	0.002	a	0.000	
Hg (ous)	0.75	i	...	0.002	v. sl.	s. d.	v. sl.	d.	a	a	0.06	i
Hg (ic)	25	0.5	...	3.6	v. sl.	s.	v. sl.	v. s	a	a	d.	i
Cu	7.2	v. s.	a	71	i	sl. s.	...	v. s.	0.0025	a	31	i
Bi	d. i.	d.	i	d	i	...	i. d.	d.	a	a	d.	i
Cd	v. s.—	57	i	140	a	4.35	80	109	0.003	a	75	a
Sn (ous)	d.	85	...	84	...	v. s.	1.32	d.	...	i	18	i
Sn (ic)		s. d.	...	s	s	d.	d.	d.	...	i	v. s.	i
Sb (o		d.	...	600	...	384	d.	...	...	i	d.	i

Solubility Products of some Important Substances

Salts		*Solubility Product*	*Remarks*
Silver bromide	..	3.5×10^{-13}	
Silver cyanide	..	2.2×10^{-12}	$[Ag][Ag(CN)_2]$
Silver chloride	..	1.56×10^{-10}	
Silver chromate	..	2.6×10^{-12}	$[Ag]^2[CrO_4]$
Silver iodide	..	1.7×10^{-17}	
Silver hydroxide	..	2.2×10^{-8}	
Silver sulphide	..	1.6×10^{-49}	$[Ag]^2[S]$
Aluminium hydroxide	..	3.7×10^{-15}	$[Al][OH]^3$
Barium carbonate	..	8.1×10^{-9}	
Barium chromate	..	2.3×10^{-10}	
Barium sulphate	..	1.2×10^{-10}	
Calcium carbonate	..	0.9×10^{-8}	
Calcium fluoride	..	3.2×10^{-11}	$[Ca][F]^2$
Calcium oxalate	..	2.6×10^{-9}	
Calcium sulphate	..	6.1×10^{-5}	
Cobalt sulphate	..	3.0×10^{-26}	
Cupric sulphide	..	8.5×10^{-45}	
Cuprous sulphide	..	2.6×10^{-47}	$[Cu]^2[S]$
Ferrous hydroxide	..	1.6×10^{-14}	$[Fe][OH]^2$
Ferrous sulphide	..	1.5×10^{-19}	
Ferric hydroxide	..	1.1×10^{-36}	$[Fe][OH]^3$
Mercurous chloride	..	2.0×10^{-18}	$[Hg_2][Cl]^2$
Mercuric sulphide	..	4.0×10^{-53}	
Magnesium carbonate	..	2.6×10^{-5}	
Magnesium hydroxide	..	1.2×10^{-11}	$[Mg][OH]^2$
Manganese hydroxide	..	4×10^{-14}	$[Mn][OH]^2$
Manganese sulphide	..	7.0×10^{-19}	
Nickel sulphide	..	3.0×10^{-21}	
do II	..	1.0×10^{-26}	
Lead chromate	..	1.8×10^{-14}	
Lead sulphate	..	1.0×10^{-8}	
Lead sulphide	..	4.2×10^{-28}	
Strontium carbonate	..	1.6×10^{-9}	
Strontium sulphate	..	2.8×10^{-7}	
Zinc hydroxide	..	1.8×19^{-14}	$[Zn][OH]^2$
Zinc sulphide	..	1.2×10^{-23}	

Dissociation Constants

Acids				*Bases*
Arsenious acid		..	6.0×10^{-10}	Ammonia 1.9×10^{-5}
Boric acid		..	6.6×10^{-10}	
Carbonic acid	I	..	3.0×10^{-7}	
—	II	..	6.0×10^{-11}	
Phosphoric acid	I	..	1.1×10^{-2}	
—	II	..	2.0×10^{-7}	
—	III	..	3.6×10^{-13}	
Acetic acid	I	..	1.8×10^{-5}	
Oxalic acid		..	3.8×10^{-2}	
—	II	..	7.0×10^{-5}	
Hydrogen sulphide	I	..	9.0×10^{-8}	

Ionisation Constants of Complex ions

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6{\cdot}8 \times 10^{-5} \qquad \frac{[HgCl_2][Cl^-]^2}{[HgCl_4^=]} = 1.0 \times 10^{-2}$$

$$\frac{[Ag^+][S_2O_3^=]}{[AgS_2O_3^-]} = 1.0 \times 10^{-13} \qquad \frac{[Hg^{++}][Cl^-]^4}{[HgCl_4^=]} = 3{\cdot}0 \times 10^{-17}$$

$$\frac{[Ag^+][CN^-]^2}{[Ag(CN)_4^-]} = 1.0 \times 10^{-21} \qquad \frac{[Hg^{++}][I^-]}{[HgI_4^=]} = 5{\cdot}0 \times 10^{-31}$$

$$\frac{[Cu^+][CN^-]^4}{Cu(CN)_4^=} = 5{\cdot}0 \times 10^{-28}$$

FACTORS

Sought	Weighed as	×Factor F	Log F
Ag	AgCl	0·7526	$\bar{1}.8766$
Cl	AgCl	0·2474	$\bar{1}{\cdot}3934$
Ba	$BaSO_4$	0·5885	$\bar{1}{\cdot}7697$
SO_4	$BaSO_4$	0·4115	$\bar{1}{\cdot}6144$
S	$BaSO_4$	0·1373	$\bar{1}{\cdot}1378$
Cu	CuO	0·7989	$\bar{1}{\cdot}9025$
Fe	Fe_2O_3	0·6994	$\bar{1}{\cdot}8447$
Pb	$PbSO_4$	0·6833	$\bar{1}{\cdot}8346$
Zn	ZnO	0·8034	$\bar{1}{\cdot}9049$
Cr	Cr_2O_3	0·6841	$\bar{1}{\cdot}8352$
Ca	CaO	0·7147	$\bar{1}.8541$
Al	Al_2O_3	0·5291	$\bar{1}{\cdot}7236$
Mg	$Mg_2P_2O_7$	0·2184	$\bar{1}{\cdot}3393$

GRAM EQUIVALENT

For Normal Solutions

Acidimetry :

Na_2CO_3	...	... 53·06 g.
NaOH	...	... 40·00 g.
Oxalic acid	...	... 63·04 g.
HCl	...	... 36·46 g.
H_2SO_4	...	... 49·04 g.
$NaHCO_3$	...	... 84·00 g.
$Ba(OH)_2 \cdot 8H_2O$	...	... 157·75 g.

Oxidation :

$K_2Cr_2O_7$	...	... 49·03 g.
KIO_3	...	... 30·67 g.
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	...	... 392·13 g.
$H_2C_2O_4 \cdot 2H_2O$	...	... 63·04 g.
$KMnO_4$	...	... 31·606 g.
$HgCl_2$ to $HgCl$	...	... 271·52 g.
Fe (ous ion)	...	... 55·84 g.
Iodine	...	... 126·92 g.
Hypo, $Na_2S_2O_3 \cdot 5H_2O$	...	... 248·19 g.
As_2O_3	...	... 49·45 g.
$CuSO_4 \cdot 5H_2O$	...	... 249·71 g.

Precipitation

KCl	...	... 75·55 g.
$AgNO_3$	...	... 169·89 g.
NaCl	...	... 58·45 g.
KCNS	...	... 97·17 g.

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences 1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences 1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences 1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	2855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	50 7	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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